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(54) **New cyclohexane derivatives having plant-growth regulating activities, and uses of these derivatives.**

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Description

Field of the Invention

This invention relates to a new cyclohexane derivative, more particularly new derivative of 3,5-dioxocyclohexanecarboxylic acid, having high plant-growth regulating activities and to process for the preparation of said cyclohexane derivatives. This invention also relates to a plant-growth regulating composition comprising said cyclohexane derivative as the active ingredient, and further to a method of regulating the growth of a plant using said cyclohexane derivative.

Background of the Invention

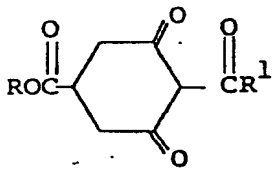
Various chemical compounds have been used for regulation of the growth of plants with a chemical substance, so called for the purpose of "chemical control" of the plant-growth. For example, maleic hydrazide (MH), N,N-dimethylaminosuccinic amide (known as Daminozide or B-Nine) and 2-chloroethyl trimethyl ammonium chloride (known as Chlormequat or CCC) have been employed fore retardation of plant-growth, for control of emergence of sideshooting or for prevention of lodging of plants. These known compounds, however, have various drawbacks that their uses are restricted in respect of the locus, plants and time which can effectively be treated with them, that their plant-growth regulating effects are insufficient or unstable, that they are phytotoxic, and/or they are too expensive.

We have made extensive studies in an attempt to provide new plant-growth regulators which are free from the aforementioned drawbacks of the known plant-growth regulators. As a result, we have now found that certain new cyclohexane derivatives which we have now newly synthetized exhibit some remarkable plant-growth regulating effects and are free from the drawbacks as described above.

EP—A—126 713, published after the filing date of the present patent application, discloses compounds which are in part similar to those being claimed here, as well as their use as herbicides and plant-growth regulators.

Detailed Description of the Invention

According to an aspect of this invention, therefore, there is provided a cyclohexane compound of the general formula:



(I)

wherein (i) R is a hydrogen atom or an alkyl group and then R^1 is an alkyl group, an unsubstituted or substituted benzyl group, a phenethyl group, a phenoxymethyl group or a 2-thienylmethyl group, or (ii) R is an alkylthioalkyl group, a phenyl group or substituted phenyl group and then R^1 is an unsubstituted or substituted benzyl group, a phenethyl group, a phenoxymethyl group or a 2-thienylmethyl group; or a salt of said cyclohexane compound (I) with an inorganic or organic cation; with the proviso that when a compound of formula I is such that R is hydrogen or alkyl and R^1 is alkyl, then said compound is in the form of a salt thereof.

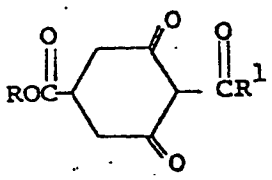
The alkyl group which R may represent in the general formula (I) includes those containing 1 to 8 carbon atoms, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, and iso-pentyl groups.

The alkyl group which R^1 may represent includes those of 1 to 8 carbon atoms, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, n-pentyl, n-hexyl, n-heptyl and n-octyl groups.

The substituent on the unsubstituted phenyl group which R may represent, as well as the substituent on the substituted benzyl group which R^1 may represent may be a lower alkyl group of 1 to 4 carbon atoms such as methyl; halo group such as chloro; and a lower alkoxyl group of 1 to 4 carbon atoms such as methoxy.

Typical examples of the cyclohexane compounds of the general formula (I), which are herein claimed or whose salts are herein claimed, are listed in Table 1 below, where the physical properties of each compound are also indicated.

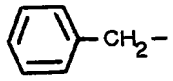
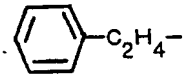
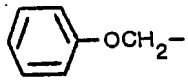
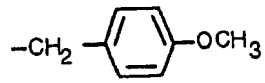
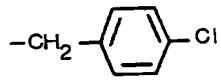
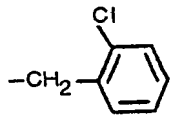
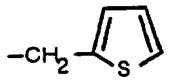
TABLE 1



(I)

Compound No.	R	R^1	Physical Properties
1	C_2H_5—	CH_3—	m.p. 40 ~ 42°C
2	n-C_3H_7—	〃	m.p. 43 ~ 44°C
3	i-C_3H_7—	〃	m.p. 98 ~ 100°C
4	n-C_4H_9—	〃	n_D^{20} = 1.4991
5	i-C_4H_9—	〃	m.p. 39 ~ 40°C
6	s-C_4H_9—	〃	m.p. 36 ~ 37°C
7	t-C_4H_9—	〃	m.p. 76 ~ 77°C
8	CH_2—	C_2H_5—	m.p. 49 ~ 50°C
9	C_2H_5—	〃	m.p. 55 ~ 56°C
10	n-C_3H_7—	〃	n_D^{20} = 1.4960
11	i-C_3H_7—	〃	m.p. 55 ~ 56°C
12	H—	〃	m.p. 98 ~ 99°C
13	〃	n-C_3H_7—	m.p. 116 ~ 119°C
14	CH_3—	〃	n_D^{20} = 1.5025
15	C_2H_5—	〃	m.p. 34 ~ 35°C
16	n-C_3H_7—	〃	n_D^{20} = 1.5010
17	i-C_3H_7—	〃	n_D^{20} = 1.4941
18	n-C_4H_9—	〃	n_D^{20} = 1.4930
19	i-C_4H_9—	〃	n_D^{20} = 1.4958
20	s-C_4H_9—	〃	n_D^{20} = 1.4893
21	i-C_5H_{11}—	〃	n_D^{20} = 1.4885
22	C_2H_5—	i-C_3H_7—	n_D^{20} = 1.4898
23	〃	n-C_4H_9—	n_D^{20} = 1.4943
24	〃	i-C_4H_9—	n_D^{20} = 1.4948
25	〃	n-C_5H_{11}—	n_D^{20} = 1.4878
26	〃	n-C_6H_{13}—	n_D^{20} = 1.4803

TABLE 1

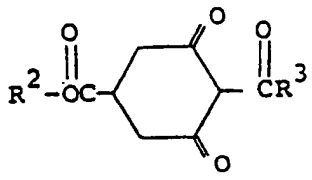
Compound No.	R	R¹	Physical Properties
27	〃	n-C_7H_{15}—	n_D^{20} = 1.4773
28	〃	n-C_8H_{17}—	n_D^{20} = 1.1650
29	C_2H_5—		m.p. 67 ~ 68°C
30	〃		m.p. 80 ~ 81°C
31	〃		m.p. 66 ~ 68°C
32	H—	CH_3—	m.p. 139 ~ 141°C
33	CH_3—	〃	m.p. 77 ~ 77.5°C
34	t-C_4H_9—	C_2H_5—	m.p. 67 ~ 69°C
35	C_2H_5—		m.p. 74 ~ 75°C
36	〃		m.p. 78 ~ 79°C
37	〃		n_D^{20} = 1.5610
38	〃		m.p. 61 ~ 63°C

Amongst the particular compounds of Table 1, the following compounds are preferred in this invention.

(1) Compound No. 8: 3,5-dioxo-4-propionylcyclohexanecarboxylic acid methyl ester;
(2) Compound No. 9: 3,5-dioxo-4-propionylcyclohexanecarboxylic acid ethyl ester;
(3) Compound No. 10: 3,5-dioxo-4-propionylcyclohexanecarboxylic acid n-propyl ester;
(4) Compound No. 13: 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid;
(5) Compound No. 15: 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid ethyl ester;
(6) Compound No. 16: 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid n-propyl ester;
(7) Compound No. 17: 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid isopropyl ester;
(8) Compound No. 18: 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid n-butyl ester;
(9) Compound No. 21: 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid isopentyl ester;
(10) Compound No. 22: 3,5-dioxo-4-isobutyrylcyclohexanecarboxylic acid ethyl ester; and
(11) Compound No. 32: 3,5-dioxo-4-isobutyrylcyclohexanecarboxylic acid.

For plant-growth regulators to be applied onto grass swards, it is usually required that they should have a particularly improved safety in their stimulus for human's skin and eye since they are frequently used for treatment of swards planted in golf links, parks or yards so that they are likely to be brought into direct contact with human bodies.

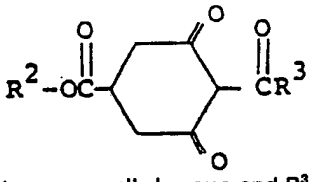
Through our further studies, we have found that such a class of the new cyclohexane derivative of the general formula (I) which is represented by the following general formula (Ia)



(Ia)

wherein R^2 represents a hydrogen atom or an alkyl group and R^3 represents an alkyl group can provide such a salt with an inorganic or organic cation which exhibits a significantly reduced stiumuls to skin and eye of the animal or human, as compared to the similar salt of the another classes of the new cyclohexane derivative according to the general formula (I), with retaining their excellent plant-growth regulating effects.

According to a preferred embodiment of the first aspect of this invention, therefore, there is provided a salt of cyclohexane compound of the general formula:

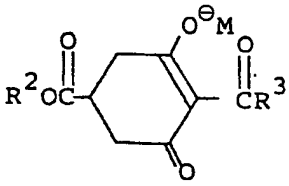


(Ia)

wherein R^2 represents a hydrogen atom or an alkyl group and R^3 represents an alkyl group.

The salt of the new cyclohexane compound according to the general formula (Ia) may be any of the following three types:

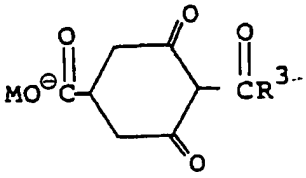
(i) A salt of the cyclohexane compound represented by the general formula:



(Ib)

wherein R^2 and R^3 are as defined above and M represents an organic or inorganic cation.

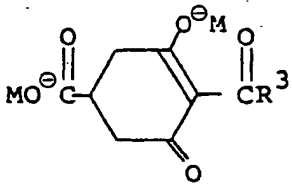
(ii) A salt of the cyclohexane compound represented by the general formula:



(Ic)

wherein R^3 and M are as defined above.

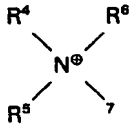
(iii) A salt of the cyclohexane compound represented by the general formula:



(Id)

wherein R^3 and M are as defined above.

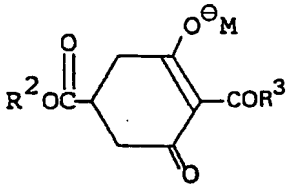
In the above formulae (Ia), (Ib), (Ic) and (Id), R^2 is as defined hereinbefore and preferably is a hydrogen atom or an alkyl group such as methyl, ethyl, n-propyl, iso-propyl, n-butyl or iso-butyl, R^3 is as defined hereinbefore and preferably is an alkyl group such as mentioned just above, and M stands for an organic or inorganic cation. The inorganic cation here may be the cation of an alkali metal (including ammonium cation), an alkaline earth metal, aluminium, copper, nickel, manganese, cobalt, zinc, iron and silver. The organic cation may be a substituted ammonium ion represented by the formula:



wherein R^4, R^5, R^6 and R^7 each represents a hydrogen atom or an alkyl, a hydroxyalkyl, an alkenyl, benzyl, a halogen-substituted benzyl, pyridyl or an alkyl-substituted pyridyl group, or R^4 and R^5 taken together form a polymethylene group which may optionally be interrupted by an oxygen atom.

Typical examples of the various salts of the formula (Ib), (Ic) or (Id) according to this invention are shown in Tables 2—4 below.

TABLE 2



(Ib)

Compound No.	R^2	R^3	M	Physical Properties
39	CH_3	CH_3	$H_2N^{\oplus}(C_2H_4OH)_2$	m.p. 88 ~ 91°C
40	"	C_2H_5	"	m.p. 85 ~ 86°C
41	"	"	$H_2N^{\oplus}(CH_2\underset{\displaystyle OH}{\underset{\vert}{C}}HCH_3)_2$	m.p. 90 ~ 92°C
42	"	n-C_3H_7	$H_2N^{\oplus}(C_2H_4OH)_2$	m.p. 62 ~ 64°C
43	C_2H_5	CH_3	"	(see Table 5 given later)
44	"	"	$H_2N^{\oplus}(C_2H_5)_2$	(see Table 5)
45	"	C_2H_5	"	(see Table 5)
46	"	"	$H_2N^{\oplus}(n\text{-}C_3H_7)_2$	m.p. 76 ~ 80.5°C
47	"	"	$H_2N^{\oplus}(i\text{-}C_3H_7)_2$	m.p. 42 ~ 44.5°C
48	"	"	$H_2N^{\oplus}(C_2H_4OH)_2$	m.p. 76 ~ 78°C (see Table 5)
49	"	"	$H_2N^{\oplus}(CH_2\underset{\displaystyle OH}{\underset{\vert}{C}}HCH_3)_2$	m.p. 91 ~ 94°C
50	"	"	$H_2N^{\oplus}(CH_2CH{=}CH_2)_2$	(see Table 5)
51	"	"	$H_2N^{\oplus}(n\text{-}C_4H_9)_2$	m.p. 94 ~ 96°C
52	"	"	$H_2N^{\oplus}(i\text{-}C_4H_9)_2$	(see Table 5)
53	"	"	$H_2N^{\oplus}(CH_2\underset{\displaystyle (CH_2)_3\,CH_3}{\underset{\vert}{C}}H{-}C_2H_5)_2$	refractive index n_D^{25} = 1.4965

TABLE 2

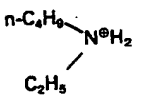
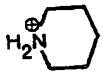
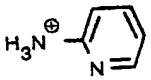
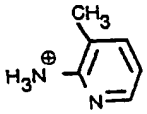
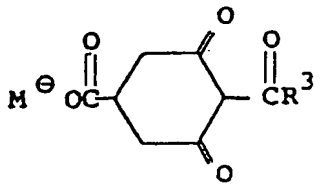
Compound No.	R^2	R^3	M	Physical Properties
54	"	"	$H_2N^{\oplus}(n\text{-}C_{12}H_{25})_2$	m.p. 62 ~ 63°C
55	"	"		m.p. 63 ~ 65°C
56	"	"	$H_3N^{\oplus}(t\text{-}C_4H_9)$	refractive index $n_D^{20} = 1.5069$
57	"	"	$HN^{\oplus}(C_2H_5)_3$	refractive index $n_D^{25} = 1.5098$
58	"	"	$HN^{\oplus}(C_2H_4OH)_3$	m.p. 53 ~ 56°C
59	"	"		refractive index $n_D^{25} = 1.5505$
60	"	"		m.p. 55 ~ 56°C
61	"	"		m.p. 55 ~ 57°C
62	"	"		m.p. 75 ~ 76°C
63	"	"		m.p. 67 ~ 68°C
64	"	"	$\frac{1}{2}\ Mg^{2\oplus}$	m.p. 184 ~ 188°C
65	"	"	$\frac{1}{2}\ Cu^{2\oplus}$	m.p. 203 ~ 206°C-(decomp.)
66	"	"	$\frac{1}{2}\ Ni^{2\oplus}$	m.p. >290°C
67	"	"	$\frac{1}{2}\ Ca^{2\oplus}$	(see Fig. 1)
68	"	"	$Na^{\oplus}$	(see Fig. 2)
69	"	"	$K^{\oplus}$	(see Fig. 3)
70	"	$n\text{-}C_3H_7$	$H_2N^{\oplus}(C_2H_5)_2$	m.p. 63 ~ 65°C
71	"	"	$H_2N^{\oplus}(C_2H_4OH)_2$	m.p. 51 ~ 53°C
72	"	"	$Na^{\oplus}$	(see. Fig. 4)
73	"	"	$K^{\oplus}$	(see Fig. 5)
74	"	"	$\frac{1}{2}\ Ca^{2\oplus}$	m.p. 157 ~ 159°C
75	"	"	$\frac{1}{3}\ Fe^{3\oplus}$	refractive index $n_D^{20} = 1.5475$
76	"	"	$\frac{1}{3}\ Al^{3\oplus}$	refractive index $n_D^{20} = 1.5294$
77	$i\text{-}C_3H_7$	C_2H_5	$H_2N^{\oplus}(C_2H_4OH)_2$	m.p. 71 ~ 73°C

TABLE 3



(Ic)

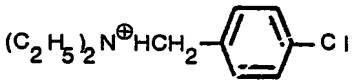
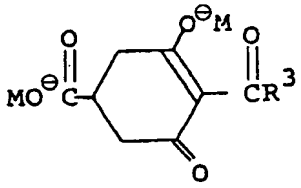
Compound No.	R^3	M	Physical Properties
78	n-C_3H_7	$HN^{\oplus}(C_2H_5)_3$	refractive index n_D^{20} = 1.5182
79	"	$(HOC_2H_4)N^{\oplus}(CH_3)_3$	refractive index n_D^{20} = 1.5118
80	"	$H_2N^{\oplus}(C_2H_5)_2$	refractive index n_D^{20} = 1.5172
81	"	$H_2N^{\oplus}(C_2H_4OH)_2$	refractive index n_D^{20} = 1.5330
82	C_2H_5	$H_3N^{\oplus}$(n-C_3H_7)	(see Fig. 6)
83	"		refractive index n_D^{20} = 1.5392
84	"	$H_2N^{\oplus}(C_2H_4OH)_2$	refractive index n_D^{20} = 1.5283
85	"	$Na^{\oplus}$	melting point 225°C (decomp.)
86	"	$K^{\oplus}$	m.p. 200 ~ 205°C

TABLE 4



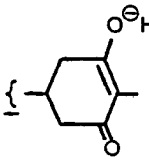
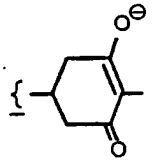
(Id)

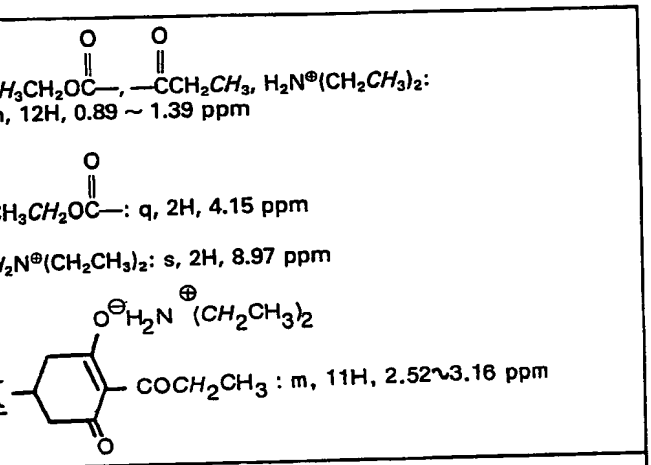
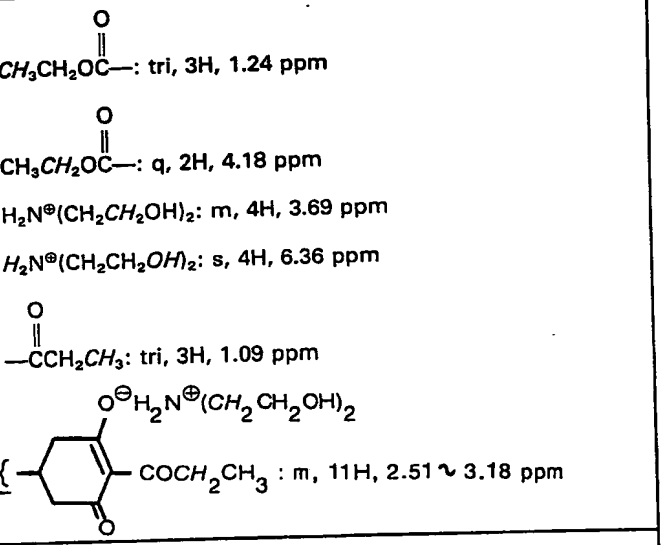
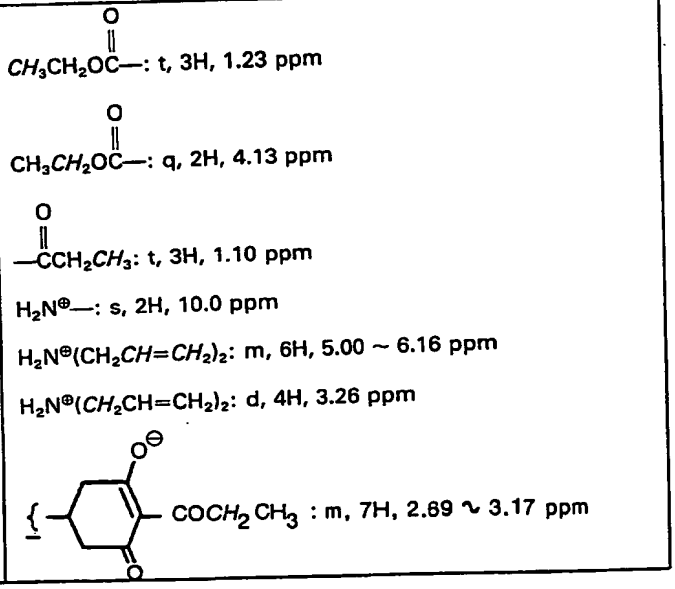
Compound No.	R^3	M	Physical Properties
87	C_2H_5	$Na^{\oplus}$	m.p. 240°C (decomp.)
88	"	$H_2N^{\oplus}(C_2H_4OH)_2$	refractive index n_D^{20} = 1.5351 (see Fig. 7)
89	n-C_3H_7	$Na^{\oplus}$	refractive index n_D^{20} = 1.5261

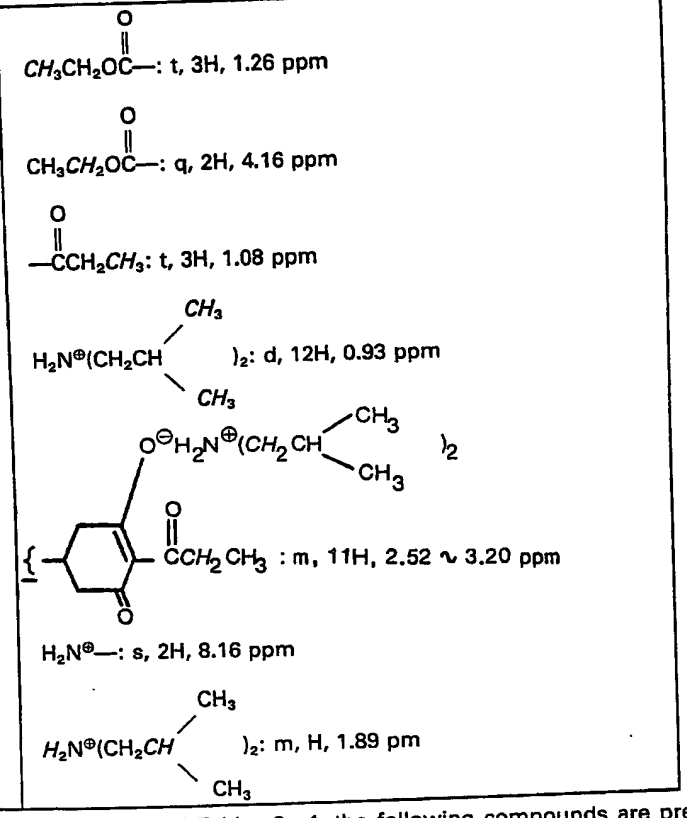
In the accompanying drawings, Figs. 1, 2, 3, 4, 5, 6 and 7 show infrared absoprtion spectra of Compound Nos. 67, 68, 69, 72, 73, 82 and 88, listed in Tables 2—3, respectively.

Table 5 below shows the analytical results of nucler magnetic resonance spectra (in $CDCl_3$) of some of the compounds according to this invention which are indicated with reference to Compound Number as shown in Tables 2—3.

TABLE 5

Compound No.	Characteristic peaks for particular radicals in N.M.R. Spectra
43	$CH_3CH_2OC(=O)$—: tri, 3H, 1.10 ppm $CH_3CH_2OC(=O)$—: q, 2H, 4.13 ppm —$C(=O)CH_3$: s, 3H, 2.33 ppm $H_2N^{\oplus}(CH_2CH_2OH)_2$: m, 4H, 3.66 ppm $H_2N^{\oplus}(CH_2CH_2OH)_2$: s, 4H, 4.46 ppm  : m, 9H, 2.50—3.06 ppm
44	$CH_3CH_2OC(=O)$—, $H_2N^{\oplus}(CH_2CH_3)_2$: tri, 9H, 1.23 ppm $CH_3CH_2OC(=O)$—; q, 2H, 4.13 ppm —$C(=O)CH_3$: s, 3H, 2.33 ppm $H_2N^{\oplus}(CH_2CH_3)_2$: q, 4H, 3.30 ppm $H_2N^{\oplus}(CH_2CH_3)_2$: s, 2H, 9.13 ppm  : m, 5H, 2.52∿2.82 ppm

45	
48	
50	

52	

Amongst the particular compounds of Tables 2—4, the following compounds are preferred in this invention:

(12) Compound No. 48: [Bis-(2-hydroxyethyl)]ammonium salt of ethyl, 3,5-dioxo-4-propionyl-cyclohexanecarboxylate.

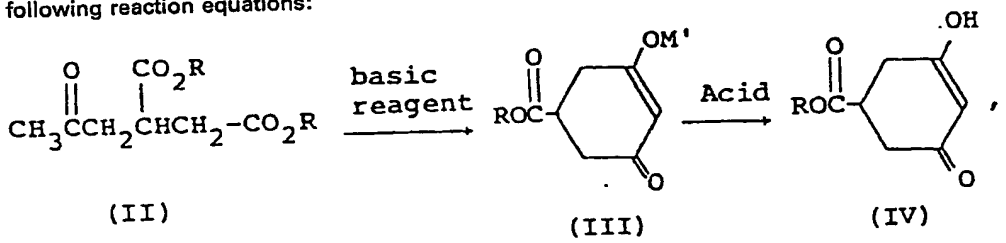
(13) Compound No. 68: Sodium salt of ethyl 3,5-dioxo-4-propionyl-cyclohexanecarboxylate.

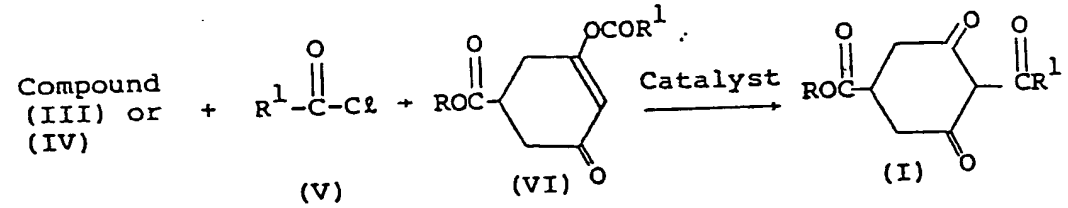
(14) Compound No. 87: Di-sodium salt of 3,5-dioxo-4-propionylcyclohexanecarboxylic acid.

(15) Compound No. 88: Bis-{[bis-(2-hydroxyethyl)]ammonium} salt of 3,5-dioxo-4-propionyl-cyclohexanecarboxylic acid.

(16) Compound No. 49: [Bis-(2-hydroxypropyl)]ammonium salt of ethyl 3,5-dioxo-4-propionyl-cyclohexanecarboxylate.

The compounds of the general formula (I) can be prepared by a method briefly depicted according to the following reaction equations:





wherein R and R^1 are as defined hereinabove for the general formula (I) and M' is an alkali metal.

The 3,5-dioxo-cyclohexanecarboxylic acid alkyl ester alkali metal salt of the above formula (III) may be prepared by reacting an acetonylsuccinic acid di-alkyl ester compound of the formula (II) with a basic reagent in a suitable solvent. This cyclization reaction can be carried out at a temperature ranging from room temperature to the boiling point of the solvent used for period of 1 to 10 hours. The basic reagent to be used in this reaction includes an alkali metal alcoholate such as sodium methylate, sodium ethylate and potassium tert-buthoxide or an alkali metal hydride such as sodium hydride. Examples of the solvent used here may be methanol, ethanol, benzene, toluene, xylene, N,N-dimethylformamide, dimethylsulfoxide and dimethylcellosolve.

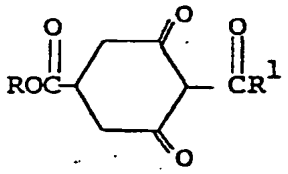
The 3,5-dioxo-cyclohexanecarboxylic acid or its alkyl ester compound of the formula (IV) can be made by treatment of the compound (III) prepared as above with an acid such as hydrochloric acid.

The compound of the above formula (VI) can be prepared by condensing the compound (III) or (IV) in an inert organic solvent with an organic acid chloride of the formula (V) where R^1 is as defined hereinbefore, in the presence or absence of γ-picoline and in the presence or absence of a base. This condensation reaction may be carried out at a temperature in the range of from −20°C to the boiling point of the solvent when used, and preferably at or below ambient temperature. The reaction time may vary from 10 minutes to 7 hours depending upon the reaction conditions employed. The base which may optionally be used in this reaction includes any of such acid-binding agents which are generally employed for the conventional dehydrohalogenation, for examples, organic bases such as trimethylamine, triethylamine, diethylamine, dimethylamine or pyridine and inorganic bases such as sodium or potassium hydroxide. The solvent available for this reaction may include water and/or organic solvents such as toluene, benzene, xylene, dichloromethane, 1,2-dichloroethane, chloroform, carbon tetrachloride, N,N-dimethylformamide, dimethylsulfoxide and methylcellosolve. This condensation reaction is conveniently performed with the aid of γ-picoline which will act as phase transition catalyst when using water and organic solvent as the reaction medium.

The new compound of the formula (I) according to this invention can be produced by subjecting the intermediate compound of the above formula (VI) to a rearrangement reaction in the presence of a catalyst and an organic solvent at a temperature from room temperature to the boiling point of the solvent for a period of 1 to 10 hours. The catalyst to be used for this rearrangement reaction includes pyridine derivatives such as 4-N,N-dimethylaminopyridine, 4-N,N-diethylaminopyridine and 4-pyrolidinoaminopyridine; or N-alkylimidazole derivatives such as N-methylimidazole and N-ethylimidazole.

The new compound (I) of this invention can be prepared without isolation or purification of said intermediate compounds (III), (IV) and (VI).

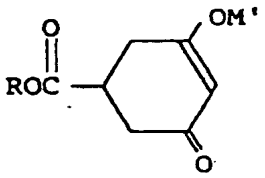
According to a second aspect of the this invention, therefore, there is provided a process for the process for the production of a cyclohexane compound of the general formula (I):



(I)

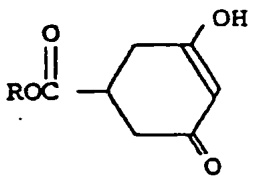
which comprises the steps of:

(a) reacting a compound of the formula (III):



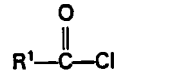
(III)

or a compound of the formula (IV):



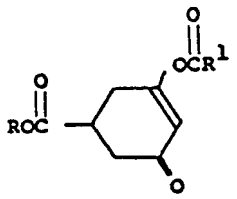
(IV)

wherein R is as defined above and M' is an alkali metal atom, with an organic acid chloride compound of the formula (V):



(V)

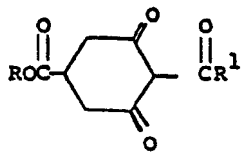
wherein R^1 is as defined above, in an organic solvent and/or water as the reaction medium in the presence or absence of a base as an acid-binding agent to produce the compound of the formula (VI):



(VI)

wherein R and R^1 are as defined above.

(b) subjecting the compound of the formula (VI) to an intermolecular rearrangement in the presence of a catalyst which is chosen from 4-N,N-dimethylaminopyridine, 4-N,N-diethylaminopyridine, 4-pyrolidinoaminopyridine, N-methylimidazole and N-ethylimidazole to produce the compound of the formula (I):

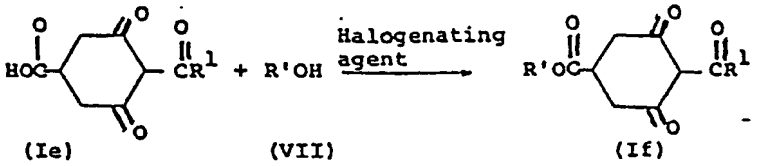


(I)

wherein R and R^1 are as defined above, and

(c) if appropriate, reacting the compound of the formula (I) with an inorganic or organic cation to produce the salt of the compound (I) with said inorganic or organic cation.

As an alternative, such new compounds of the formula (I) where R is an alkyl group may be prepared by esterification of the corresponding free carboxylic acid compound according to the following briefed reaction scheme:



(Ie) (VII) (If)

wherein R' represents an alkyl group and R^1 is as defined hereinbefore in the formula (I).

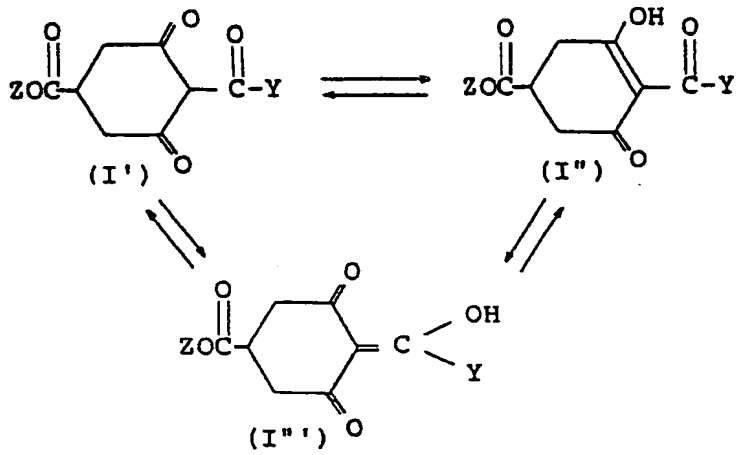
Thus, the compound of the formula (If) can be produced by a method comprising the reaction of the compound of the formula (Ie) with a halogenating agent in the presence or absence of a solvent and in the presence or absence of a base as an acid-binding agent, followed by a further esterification reaction of the acid halide derivative as formed with an alkanol (R'OH) of the formula (VII) in the presence or absence of a base. The reaction with the halogenating agent may be conducted at a temperature ranging from −20°C to the boiling point of the halogenating agent or of the solvent when used, and preferably at a temperature of from −10°C to 100°C for a period of 10 minutes to 7 hours to give an acid halide derivative of the compound (Ie). The halogenating agent to be used for the above purpose may be thionyl chloride, phosphorus trichloride, phosphorus pentachloride and phosphorus oxychloride. As the solvent which may be used for the halogenation reaction, there may be mentioned dichloromethane, chloroform, carbon tetrachloride, benzene, toluene, xylene and the like.

The subsequent reaction of esterifying the acid halide derivative with the alkanol (VII) may be carried out at a temperature of −20°C to 100°C for a time of 10 minutes to 48 hours. The base which is conveniently used for the halogenation and esterification includes those which have generally been employed for the conventional dehydrohalogenation as the acid-binding agent in the art and may be selected from organic bases such as triethylamine, pyridine, N,N-dimethylaminopyridine and N,N-dimethylaniline; and inorganic bases such as sodium hydroxide, potassium carbonate and sodium bicarbonate. The esterification with the alkanol (VII) may be conducted after or without separation of the intermediate acid halide derivative from the reaction medium.

The salts of the new cyclohexane compounds of the formula (I) or (Ia) acording to the invention can be prepared as follows:

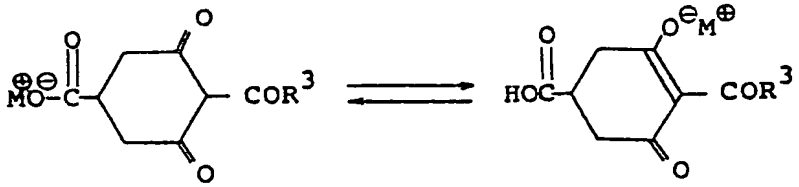
Thus, for example, an organic or inorganic salt of the new cyclohexane compound may be produced by reacting in an organic solvent a compound of the general formula (I) or (Ia) with one or two or more equivalent proportions of a salt-forming reagent which is chosen from a primary, secondary or tertiary amine, a metal alcoholate, or a metal salt such as a chloride, sulfate, nitrate, acetate or carbonate; or hydride or hydroxide of a metal, for example, an alkali metal such as sodium, potassium; an alkaline earth metal such as calcium, magnesium, barium; aluminium, nickel, copper, manganese, cobalt, zinc, iron or silver. When the compound (I) or (Ia) is reacted with one equivalent proportion of the salt-forming reagent, either the salt formed will be in the form of the salt of the general formula (Ib) as indicated in Table 2 when the group R or R^2 in the compound of the formula (I) or (Ia) is alkyl, or the salt formed will be in the form of the salt of the general formula (Ic) as indicated in Table 3 when R or R^2 is hydrogen in the compound (I) or (Ia). If two or more equivalent proportions of the salt-forming reagent is reacted with the compound (I) or (Ia), the salt as formed will take the form of the general formula (Id) as indicated in Table 4, when R or R^2 is a hydrogen atom in the compound (I) or (Ia).

The new compounds of the formula (I) or (Ia) according to this invention may possibly undergo a tautomerism and may be present in the form of tautomeric isomers as shown below, which fall within the scope of this invention.

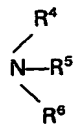


wherein Z denotes R or R^2 as defined hereinbefore and Y denotes R^1 or R^3 as defined hereinbefore.

Further, in an aqueous solution, the new compound salt of the formula (Ib) or (Ic) according to this invention may possibly change as shown below:

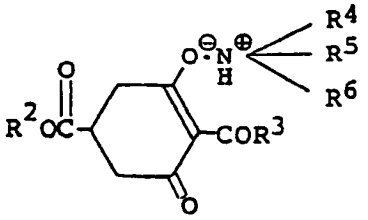


It may be added that when the cyclohexane compound of the formula (Ia) where R^2 is an alkyl group, is reacted with a primary, secondary or tertiary amine which may be represented by the formula

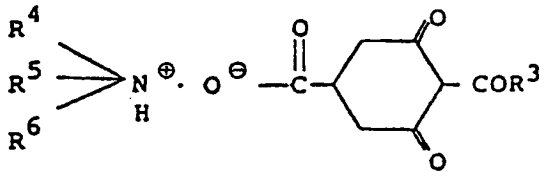


(VIII)

where R^4, R^5 and R^6 are each as defined hereinbefore but all of R^4, R^5 and R^6 cannot be each a hydrogen atom simultaneously, there is formed such salt of the compound (Ia) which may be deemed as the substituted ammonium salt of the formula



Further, when the cyclohexane compound of the formula (Ia) where R^2 is a hydrogen atom is reacted with a primary, secondary or tertiary amine of the formula (VIII), there is formed such salt of the compound (Ia) which may also be deemed as the substituted ammonium salt of the formula



In Tables 2—4, the salts of the new compounds with amine are represented as the type of the substituted ammonium salt as shown just above.

The plant-growth regulating effects of the new compounds of the general formula (I) or salts thereof as hereinbefore defined are manifested predominantly as a stunting or dwarfing effect on the vegetative growth of plants, but other various plant-growth regulating effects may be manifested by modifying the nature of plants to be treated and the means, times and rates of application of the compounds or salts. Such plant-growth regulating effects which may be induced by the new compound of this invention include promotion of rooting, reduction in risk of lodging, promotion of sideshooting and root growth, maintenance of green color of stems and leaves, promotion or delay of flowering, promotion of fruiting and ripening, and increase in resistances to temperature hindrance, to phytotoxicity caused by herbicides and to fungal or bacterial diseases. These various effects are not always manifested at a time.

The new compounds (including the salts) of this invention can control internode elongation of cereals and prevent or reduce lodging of rice, wheat, barley, maise and the other crop-plants by foliage and/or soil-treatment. Application of the compound of this invention to seedlings of aquatic rice and growing vegetables can lead to an improvement in quality, rooting after transplanting, and resistance to low temperature.

The foliage treatment with the new compound during the vegetative stage of crop plants, e.g. aquatic rice, wheat and barley also includes shortening of top leaves or improvement in leaf orientation and hence increases in light interception and utilization which will enhance the ripening and increase the overall grain yield of such crop-plants.

Moreover, the compound of this invention may suppress spindly growth of flowers, ornamental plants and horticultural plants which may be caused due to high temperature or sunshine shortage in plantation in a greenhouse.

The compounds of the invention which exhibit the above-mentioned plant-growth regulating effects are very useful not only for agricultural and horticultral treatment but also for control of plant growth in non-crop lands. For instance, when the compound of this invention is applied onto lawns in park, playing field, golf link, airport or embankment or undergrowth grasses in orchard or pasture land, it is possible to inibit the overluxuriant growth, to reduce the number of reaping and/or to facilitate the mowing operations as usually required for maintenance. Further, application of the new compound of this invention onto swards can promote sideshooting and increase the planting density of swards.

The compounds of this invention may be used as such for plant-growth regulating purposes but are more conveniently formulated into compositions for such usage. According to a third aspect of this invention, there is thus provided a plant-growth regulating composition comprising a compound of the general formula (I) or a salt thereof, as hereinbefore defined in combination with a carrier or diluent.

The invention also provides a method for regulating the growth of plant, which comprises applying an effective amount of cyclohexane compound of the formula (I) or a salt thereof of this invention to the foliage or seed of the plant to be treated or to the soil or locus where the plant to be treated is grown.

The compounds and salts can be applied in a number of ways, for example, they can be applied, formulated or unformulated, directly to the foliage of a plant, or they can be applied also to bushes and trees, to seeds or to other medium in which plants, bushes or trees are growing or are to be planted, or they can be sprayed on, dusted on or applied as a cream or paste formulation, or they can be applied as slow release granules.

The compounds are preferably used for agricultural and horticultural purposes in the form of a composition. The type of composition used in any instance will depend upon the particular purpose envisaged.

The compositions may be in the form of dusting powders or granules comprising the active ingredient and a solid diluent or carrier, for example fillers such as kaolin, bentonite, dolomite, calcium carbonate, talc, powdered magnesia, Fuller's earth, gypsum, diatomaceous earth and China clay.

The compositions may also be in the form of dispersible powders, granules or grains comprising a wetting agent to facilitate the dispersion in liquids of the powder or grains which may contain also fillers and suspending agents.

The aqueous dispersions or emulsions may be prepared by dissolving the active ingredient(s) in an inorganic solvent optionally containing wetting, dispersin or emulsifying agent(s) and then adding the mixture to water which may also contain wetting, dispersing or emulsifying agent(s). Suitable organic solvents are kerosene, cyclohexanone, methylethyl ketone, acetone, methanol and acetonitrile.

The compositions may also be in the form of liquid preparations for use as dips or sprays which are generally aqueous dispersions or emulsions containing the active ingredient in the presence of one or more of wetting agent(s), dispersing agent(s), emulsifying agent(s) or suspending agent(s). These agents can be anionic or non-ionic agents.

The compositions for use as aqueous dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient(s), and the concentrate is to be diluted with water before use.

The plant-growth regulating composition of this invention may usually be formulated into a wettable powder comprising 5 to 95%, preferably 10 to 50% by weight of the new compounds of this invention as active ingredient; 1 to 20%, preferably 5 to 10% by weight of surfactant; and 4 to 94%, preferably 40 to 85% by weight of solid carrier.

The composition of this invention may be formulated into an emulsifiable concentrate comprising 5 to 95%, preferably 20 to 70% by weight of the new compound of this invention as active ingredient; 1 to 40%, preferably 5 to 20% by weight of surfactant; and 4 to 94%, preferably 10 to 75% by weight of liquid carrier.

The composition of this invention may be made up as granules comprising 0.5 to 40%, preferably 2 to 10% by weight of the new compound of this invention as active ingredient; 1 to 20%, preferably 2 to 10% by weight of surfactant; and 40 to 98.5%, preferably 80 to 96% by weight of solid carrier. And, the composition of this invention may be formulated into dust comprising 0.5 to 10%, preferably 1 to 5% by weight of the active ingredient; and 99.5 to 90%, preferably 99 to 95% by weight of finely divided solid carrier.

The composition of this invention may also be formulated into a paste comprising 0.1 to 20%, preferably 1 to 10% by weight of the active ingredient, 1 to 20%, preferably 2 to 10% by weight of surfactant; and 60 to 98.9%, preferably 80 to 97% by weight of paste base.

The rate of application of the new compounds of this invention for use in the purposes of plant-growth regulation will normally depend on various factors, including nature of plants to be treated, application time and application means. In general, however, the rate of application may be in the range of 0.01 kg to 50 kg per hectare and preferably of 0.05 kg to 10 kg per hectare as the active ingredient.

For the purpose of preventing or reducing lodging of crop plants such as wheat, the rate of application may desirably be in a range of 0.1 kg to 1 kg per hectare as the active ingredient. For the purpose of suppressing the growth of swards in non-crop lands or undergrowth-grasses in orchards, the rate of application may be in a range of 0.5 kg to 5 kg per hectare as the active ingredient. For the purpose of regulating the growth of aquatic rice plants, the rate of application may be in the range of 0.5 kg to 5 kg per hectare as the active ingredient when it is applied to the soil, and the formulations to be applied to the foliage of aquatic rice plant may contain the active ingredient at a concentration of 100 ppm to 5000 ppm. In general, the composition of this invention may be formulated into a diluted or dilutable preparation containing the active ingredient at a concentration of 10 ppm to 10,000 ppm and preferably of 100 ppm to 5000 ppm for use in the foliage treatment.

This invention is now illustrated with reference to the following Examples to which this invention is not limited.

Example 1

Preparation of Compound No. 15, namely ethyl 3,5-dioxo-4-butyrylcyclohexanecarboxylate

To 150 ml of ethanol containing 3.4 g of sodium was added dropwise 31 g of diethyl acetonylsuccinate (or diethyl acetmethylsuccinate) over about one hour with stirring at ambient temperature. The mixture was heated under reflux for 2 hours and then cooled to room temperature, followed by distillation off of the ethanol under reduced pressure. There was thus obtained a brown viscous liquid comprising sodium salt of ethyl 3,5-dioxocyclohexanecarboxylate as formed, to which were added 100 ml of toluene, 50 ml of ice water and 0.3 g of η-picoline and then added dropwise 15 g of n-butyryl chloride at ambient temperature under agitation over about 2 hours. The resultant reaction mixture was agitated for further 30 minutes and then the toluene layer was separated, washed with water, dried and admixed with 0.8 g of 4-N,N-dimethyl-aminopyridine. The admixture was heated with agitation at a temperature of 80—90°C for 3 hours. The toluene was then distilled off from the reaction solution under reduced pressure and the residue was

chromatographed on a column of silica gel developed with benzene to give 19.5 g (55.9%) of the object compound (Compound No. 15).

Compound Nos. 1, 2 and Nos. 4—38 could be prepared by the same procedure as described in Example 1.

Example 2

Preparation of Compound No. 23, namely ethyl 3,5-dioxo-4-n-valerylcyclohexancarboxylate

2.1 g of 5-ethoxycarbonyl-cyclohexane-1,3-dione, namely ethy 3,5-dioxocyclohexanecarboxylate was dissolved in 20 ml of dichloromethane, to which was added 1.7 g of triethylamine and then added dropwise 1.9 g of n-valeryl chloride with stirring over 30 minutes. The mixture was continued to be stirred for 3 hours, and the reaction solution obtained was washed with water. The organic layer was separated from the aqueous phase, dried and concentrated to a small volume.

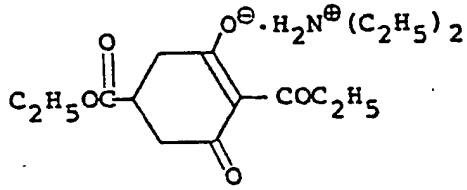
The concentrated solution was taken up in 20 ml of toluene, followed by addition of 0.6 g of 4-N,N-dimethyl-aminopyridine and heating at a temperature of 80—90°C for 4 to 5 hours. Subsequently, the toluene was removed from the reaction solution by distillation under reduced pressure, and the residue was chromatographed on silica gel using benzene as the developing solvent to yield 2.2 g (71.9%) of the aimed compound (Compound No. 33).

Compound Nos. 1—22 and Nos. 23—38 could be produced by the same procedure as stated in Example 2.

Example 3

Preparation of Compound No. 45 (see Table 2)

1.0 g of ethyl 3,5-dioxo-4-propionylcyclohexanecarboxylate was dissolved in 20 ml of chloroform, to which was then added 1.0 g of diethylamine as the salt-forming reagent. The mixture was allowed to stand at room temperature for two hours, after which the chloroform and the excess of diethylamine were distilled off from the reaction solution under reduced pressure to yield 1.3 g of the object compound (Compound No. 45) as a pale brown solid and represented by the formula



Example 4

Preparation of Compound No. 48 (see Table 2)

4.0 g of ethyl 3,5-dioxo-4-propionylcyclohexanecarboxylate was dissolved in 50 ml of ethanol and 1.7 g of diethanolamine was added to the solution, followed by stirring for 30 minutes. The ethanol was then distilled off from the reaction solution under reduced pressure to precipitate a crystal, which was washed with ethyl ether and dried to afford 5.2 g of the object compound as a pale yellow crystal having a melting point of 76—78°C.

Example 5

Preparation of Compound No. 57

1.0 g of triethylamine was added to 1.0 g of ethyl 3,5-dioxo-4-propionylcyclohexanecarboxylate dissolved in 20 ml of chloroform, and the resultant mixture was allowed to stand at ambient temperature for 2 hours. The chloroform and the excess triethylamine were distilled off from the reaction solution under reduced pressure to yield 1.4 g of the desired compound (Compound No. 57) in the form of brown viscous liquid with a refractive index $n_D^{20} = 1.5098$.

Example 6

Preparation of Compound No. 67

1.0 g of potassium salt of ethyl 3,5-dioxo-4-propionylcyclohexanecarboxylate was dissolved in water, to which was added 0.25 g of calcium chloride. The mixture was allowed to stand overnight to effect the cation-exchange reaction, after which the reaction solution was concentrated by evaporation of the water. The concentrated solution was extracted with hot ethanol and the ethanolic extract was admixed with hexane to precipitate a crystal. The latter was filtered and dried to give 0.7 g of the aimed compound as a colorless powder having a melting point of 213—215°C.

Example 7

Preparation of Compound No. 68

To 8.4 g of ethyl 3,5-dioxo-4-propionylcyclohexanecarboxylate dissolved in 80 ml of ethyl ether was added dropwise under agitation at room temperature 50 ml of ethanolic solution containing 1.4 g of sodium hydroxide. After completion of the addition, the precipitated crystal was collected by filtration and dried. Recrystallization from a mixed solvent of ethanol and hexane gave 7.2 g of the desired sodium salt compound as colorless needles with a melting point of 178.5—179.5°C.

Example 8

Preparation of Compound No. 72

2.0 g of ethyl 4-butyryl-3,5-dioxo-cyclohexanecarboxylate was added into ethanol containing 0.53 g of sodium ethylate, and the mixture was allowed to stand at room temperature for 3 hours. The ethanol was then distilled off from the reaction solution under reduced pressure to yield 2.17 g of the desired sodium salt as a pale yellow amorphous solid.

Example 9

Preparation of Compound No. 78 (see Table 3)

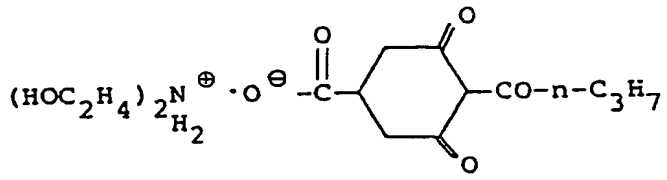
1.3 g of 4-butyryl-3,5-dioxo-cyclohexanecarboxylic acid was dissolved in 20 ml of methanol and 0.58 g of triethylamine was added to the solution. The mixture was allowed to stand overnight at ambient temperature, after which the methanol was removed from the reaction solution by evaporation under reduced pressure to leave 1.8 g of the object compound (Compound No. 78) as a pale yellow viscous liquid with $n_D^{20} = 1.5182$.

The above procedure was repeated using choline in place of the triethylamine to give Compound No. 79.

Example 10

Preparation of Compound No. 81

1.0 g of 4-butyryl-3,5-dioxo-cyclohexanecarboxylic acid was dissolved in 20 ml of methanol and 0.4 g of diethanolamine $(HOCH_2CH_2)_2NH$ was added to the solution. The mixture was allowed to stand at room temperature for 3 hours and the methanol was then removed from the reaction solution by evaporation under reduced pressure to give 1.4 g of the desired compound as a pale brown viscous liquid with $n_D^{20} = 1.5330$. This product was of the formula:



Example 11

Preparation of Compound No. 85

0.84 g of sodium bicarbonate was added to 2.1 g of 3,5-dioxo-4-propionylcyclohexanecarboxylic acid dissolved in 30 ml of ethanol, and the mixture was heated under reflux for 3 hours. The reaction solution was then cooled and filtered to leave a crystal, which was recrystallized from ethanol to give 2.2 g of the desired compound as pale yellow flakes with a melting point of 225°C (decmp.).

Example 12

Preparation of Compound No. 87 (see Table 4)

1.4 g (6.6 m moles) of 3,5-dioxo-4-propionylcyclohexanecarboxylic acid was dissolved in 30 ml of ethanol, and 0.7 g (6.6 m moles) of anhydrous sodium carbonate was added to the solution. The resultant mixture was heated under reflux for 6 hours, after which the reaction solution was cooled and filtered to leave a crystal. Recrystallization of the crystal from a mixture solvent of ethanol, methanol and hexane gave 1.3 g of the desired di-sodium salt compound as a pale yellow powder having a melting point of 240°C (decomp.).

Example 13

Preparation of Compound No. 89

2.0 g of 4-butyryl-3,5-dioxo-cyclohexanecarboxylic acid was dissolved in a mixture of methanol and water (1:1), to which was then added 0.72 g of sodium hydroxide. After complete dissolution of the latter,

the resulting solution was allowed to stand overnight, followed by removal of the methanol and water by distillation under reduced pressure. There was thus obtained 2.4 g of the object compound as a redish brown viscous liquid with $n_D^{20} = 1.5261$.

Example 14

Preparation of ethyl 3,5-dioxo-4-propionylcyclohexanecarboxylate

4.2 g of ethyl 3,5-dioxocyclohexanecarboxylate and 3.4 g of triethylamine were dissolved in 50 ml of dichloromethane, to which was added dropwise 2.9 g of propionyl chloride under stirring at room temperature. The resultant mixture was allowed to react at ambient temperature for 2 hours, after which the reaction solution was washed with water and admixed with a dilute aqueous sodium bicarbonate solution to remove the acidic matters from the reaction solution. The organic layer was then separated from the aqueous phase, dried and concentrated to a small volume. The concentration solution was taken up in 20 ml of toleune, followed by addition of 0.5 g of 4-N,N-dimethylaminopyridine and heating the mixture at 85°C for 3 hours. Thereafter, the toluene was removed from the reaction solution by distillation under reduced pressure, and the residue was chromatographed on silica gel using benzene as developing solvent to afford 2.5 g of the title compound (Compound No. 9 of Table 1) as colorless flakes having a melting point of 55—56°C.

Example 15

Preparation of ethyl 4-n-butyryl-3,5-dioxocyclohexanecarboxylate

28.8 g of sodium salt of ethyl 3,5-dioxocyclohexanecarboxylate was admixed with 100 ml of toluene and 50 ml of ice water, and to the resulting suspension was added 0.3 g of γ-picoline. To the mixture obtained was added dropwise 15 g of n-butyryl chloride with stirring over about two hours, and the resultant mixture was continued to be stirred for 30 minutes. The toluene layer was then separated from the aqueous phase, dried and concentrated to a small volume. The concentration solution was dissolved in 20 ml of toluene and 0.8 g of 4-N,N-dimethylaminopyridine was added to the solution, which was then heated at 80—90°C under agitation for 3 hours. Thereafter, the toluene was removed from the reaction solution by distillation under reduced pressure, and the residue was chromatographed on silica gel developing with benzene to yield 19.5 g of the title compound (Compound No. 15 of Table 1) as pale yellow prisms with a melting point of 34—35°C.

The following Examples 16—20 illustrate the preparation of the composition according to this invention, in which parts are all by weight.

Example 16

Wettable powder

A composition in the form of wettable powder was prepared by mixing homogeneously and grinding 10 parts of Compound No. 39, 85 parts of kieselguhr, 2 parts of sodium dinaphthylmethanesulfonate and 3 parts of sodium lignosulfonate.

Example 17

Emulsifiable concentrate

An emulsifiable concentrate was made up by mixing the ingredients, and stirring the mixture until all the constituents were dissolved.

Compound No. 40	30 parts
Cyclohexane	20 parts
Polyoxyethylenealkylaryl ether	11 parts
Calcium alkylbenzenesulfonate	4 parts
Methylnaphthalene	35 parts

Example 18

Grains

A composition in the form of grains was prepared by uniformly mixing and grinding together 5 parts of Compound No. 41, 2 parts of sodium laurylsulfate, 5 parts of sodium lignosulfonate, 2 parts of carboxymethylcellulose and 86 parts of clay, followed by addition of 20 parts of water per 80 parts of the mixture. The resultant mixture was milled and formulated into grains of 14—32 mesh size by means of an extrusion granulator.

Example 19

Dusting powder

4 parts of Compound No. 42, 5 parts of kieselguhr and 91 parts of clay were homogeneously mixed and ground together to formulate into a dusting powder.

Example 20

Paste formulation

A paste formulation was prepard by mixing uniformly 5 parts of Compound No. 43, 1 part of xylene, 5 parts of polyoxyethylenesorbitan monolaurate and 89 parts of white vaseline as paste base.

The following Examples illustrate the plant-growth regulating effects of the compounds according to this invention.

Example 21

This Example illustrates the retardation effect of the compounds of this invention on the growth of aquatic rice plants.

Aquatic rice plants ("Kinmage" Variety) at the two-leaf stage were treated with the compounds of this invention under test. Thus, the compounds were formulated into a wettable powder as prepared in Example 16 and the wettable powder was diluted with such a volume of water that 1000 l of the diluted aqueous preparations as sprayed gave the rate of application of 1 kg of the active ingredient per hectare upon the foliage treatment by spraying.

On the day of the application and 3 weeks after the application of the compounds, the length of stems and leaves of the treated plants were measured, and retardation of growth was calculated by the following equation:—

$$\text{Retardation (\%)} = \left(1 - \frac{B}{A}\right) \times 100$$

A = (Foliar length in untreated plots 3 weeks after application) — (Foliar length in untreated plots on the day of application)

B = (Foliar length in treated plots 3 weeks after application) — (Foliar length in treated plots on the day of application)

The test results are set out in Table 6 below.

TABLE 6

Compound No. tested	Retardation (%)	Compound No. tested	Retardation (%)
41	65	73	66
42	52	74	72
43	46	75	70
44	44	76	62
45	61	77	65
46	60	78	59
47	62	79	63
48	64	80	57
49	63	81	72
50	60	82	69
51	62	83	66
52	59	84	70
53	65	85	49
54	64	86	58
55	65	87	58
56	60	88	61
57	57	89	68
58	60	90	57
59	65	91	73
60	63	92	70
61	62	93	65
62	70	94	71
63	66	95	67
64	67	CCC (Comparative)	0
65	64	B-Nine (Comparative)	0
66	71	MH (Comparative)	41

The results of Table 6 indicate that rice plant height can be controlled by the application of the new compounds of this invention and thus spindly growth of rice plant can be prevented.

Example 22

This Example illustrates the stunting effect of the compounds of this invention on the growth of grass swards.

Creeping bentgrass (*Agrostis stolonifera*) ("Seaside" Variety) and Japanese lowngrass (*Zoysia japonica*) of 2 cm in height were sprayed with the diluted aqueous preparations containing the compounds of this invention. The diluted aqueous preparations as used were prepared by formulating the compounds into wettable powder as in Example 16 and diluting the wettable powder with such a volume of water that 1000 l of the diluted aqueous preparation as sprayed gave the rate of application of 1 kg of the active ingredient per hectare upon the foliage treatment by spraying.

5 Weeks after application of the compounds, assessment was made and percentage of retardation was calculated in the same way as described in Example 21. Phytotoxicity was also assessed for some of the test compounds and indicated by the following scales:

Scales	Degree of Phytotoxicity
−	Not detected
±	Small
+	Middle
++	Great
+++	Kill

The test results are shown in Table 7 below.

TABLE 7

Compound No. tested	Retardation (%)		Phytotoxicity	
	Creeping bentgrass	Japanese lowngrass	Creeping bentgrass	Japanese lowngrass
40	45	68	—	—
48	51	58	—	—
68	53	59	—	—
84	49	54	—	—
88	40	43	—	—
MH (Comparative)	—	37	++	+

From the results of Table 7 as above, it will be seen that the new compounds of this invention exert the stunting or dwarfing effects on lawn grasses for a long period without significant phytotoxic effects and without deteriously affecting the appearance (particularly the color) of the grass, so that the compounds of this invention are useful to reduce the need for mowing the grass swards.

Example 23

This Example illustrates the improvements in quality of rice seedlings by application of the compounds of this invention.

Emergent seeds of aquatic rice ("Kinmaze" Variety) were sown in a rice-planting case of 30 × 60 cm in size, then covered with soil and irrigated with water. The compounds under test were formulated into an emulsifiable concentrate as stated in Example 17 which was then diluted with water so that the diluted emulsions contained the active ingredient at the concentrations as indicated in Table 8 below. The diluted emulsions so formulated were sprayed onto the soil surface at the rate of 20 ml per case. The cases were then kept in a thermostatic chamber at 30°C for 3 days and further placed in a greenhouse. When the rice seedlings in untreated plots had reached the stage of 2.5 leaf age, the height of seedlings, leaf age and dry weights of the foliage parts (stems/leaves) and roots of the treated and untreated plants were measured. Some members of the seedlings were washed with water, and then the seedlings were transplanted into and placed at an angle of 45° in a pot flooded with water to 2 cm depth, after cutting the roots into the

constant length of 2 cm. 10 Days later, the rising angle of the seedlings and the chlorophyll content of their second leaf were determined.

The results are shown in Table 8 below, where the assessment particulars other than the rising angle are indicated in terms of the percentages based on the results obtained for the untreated plots.

It will be seen from Table 8 that the compounds of this invention can suppress the excessive growth of rice seedlings in a planting case, promote the growth of roots and accelerate the rooting of transplanted rice seedlings.

TABLE 8

Compound No. tested	Concentration (ppm) of active ingredient in the sprayed emulsion	Quality of rice seedling at the time transplantation				Quality of rice seedling 10 days after transplantation	
		Plant height (%)	Leaf age (%)	Dry weight of foliage parts (%)	Dry weight of root parts (%)	Raising angle of seedling (degree)	Chlorophyll content of second leaf (%)
						87	108
48	1000	83	104	98	110	90	113
49	1000	80	108	96	115	90	120
51	1000	85	104	98	112	90	112
64	1000	79	108	96	119	90	136
81	1000	76	108	94	119	90	139
87	1000	83	104	97	112	90	118
Untreated	—	100	100	100	100	75	100

Example 24

This Example demonstrates that the salts of the cyclohexane compounds of the formula (Ia) according to this invention have reduced influences on eyes in contact with the latter.

3 Rabbits (Female, "Japan White" Variety, 4 months-age) of which eyeballs were found to suffer from no damage by a check with 5% aqueous fluorescein sodium solution were fixed on a fixing table. 100 mg of the test compounds as such were dropped into the left eyes of the rabbits and their eyelids were closed for one second, after which the rabbits were placed in a breeding case. The right eyes were remaining untreated for control. Eye-examinations were made 24 hours and 2, 3, 4, 7, 14 and 21 days after the treatment. The stimulus responses were evaluated in respect of various observations as indicated in Table 9, and the results are set out in Table 10.

TABLE 9

Cornea

(A) Opacity-Turbidity (the most opaque region of cornea was examined) were estimated by the following scales:

Scale 1:	Sporadical or diffusive opacity occurred to such extent that iris still remained clearly visible.
Scale 2:	Opacity occurred to such extent that fine parts of iris were somewhat dimly visible.
Scale 3:	Opacity occurred to such extent that fine parts of iris were indistinct and the size of pupil is visually distinguishable with difficulty.
Scale 4:	Opacity occurred to such extent that iris was not visible.

(B) Area suffering from corneal damage (denoted as "Area" below) was scaled as follows:

Scale 1:	$0 < \text{"Area"} < \frac{1}{4}$
Scale 2:	$\frac{1}{4} \leqq \text{"Area"} < \frac{1}{2}$
Scale 3:	$\frac{1}{2} \leqq \text{"Area"} < \frac{3}{4}$
Scale 4:	$\frac{3}{4} \leqq \text{"Area"}$

A value of a product of scale (A) x scale (B) x 5 was calculated and indicated as "Evaluation scores" of stimulus to cornea in the following Table 10, but this calculated value did not extend over the maximum value 80 even for the worst case.

Iris

(A)	Scale 1:	one or more signs of acceleration of wrinkle formation, hyperemia, swelling and hyperemia of corneal surroundings in iris were detectable but reflection response of iris to light was still good.
	Scale 2:	one or more signs of no reflection response of iris to light, bleeding and wide-spread breakdown were detectable.

A value of a product of scale (A) x 5 was calculated and indicated as "Evaluation scores" of stimulus to iris in Table 10, but this calculated value did not extend over the maximum value 10 even for the worst case.

Conjuctiva

(A) Redness (only the redness developed in the eyelid conjunctiva was examined.)

Scale 1:	Acceleration of hyperemia was observed.
Scale 2:	Wide-spread, deep-color redness and difficulty in identification of vasa were observed.
Scale 3:	Wholly-spread, deep-color redness was observed.

(B) Chemosis

Scale 1:	Acceleration of chemosis (including nictitating membrane) was observed.
Scale 2:	Swelling associated with partial valgum of eyelid was observed.
Scale 3:	Eyelid closing (in about half region) associated with swelling was observed.
Scale 4:	Eyelid closing (about half to whole region) with swelling was observed.

(C) Secreta

Scale 1:	More than ordinary amount (excluding the small quantity of secreta usually observed in inner canthus of healthy animal) of secreta was observed.
Scale 2:	Secreta was formed in the amount to wet and stain eyelid and also hairs contact with eyelid.
Scale 3:	Secreta was formed in the amount to wet and stain eyelid and also the eye surroundings over a fairly wide region.

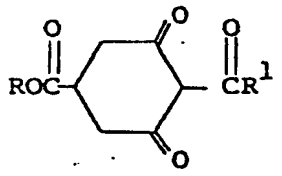
A value of a product of [scale (A) + scale (B) + scale (C)] × 2 was calculated and indicated as "Evaluation scores" in term of secreta in Table 12, but this calculated value did not extend over the maximum value 20 for the worst case.

TABLE 12

Evaluation scores of stimulus		Compound No. tested	Compound No 48			Compound No. 68			Compound No. 87			Compound No. 88			Compound No. 9 (comparative)		
		Body weight (kg)	2.5	2.6	2.5	2.7	3.0	2.7	3.0	2.6	2.5	2.5	2.5	2.1	2.7	2.6	2.6
	Cornea	24 hours	0	0	0	0	5	0	0	0	0	0	0	0	20	15	20
		2 days	0	0	0	0	0	0	0	0	0	0	0	0	20	15	20
		3 days	0	0	0	0	0	0	0	0	0	0	0	0	20	10	15
		4 days	0	0	0	0	0	0	0	0	0	0	0	0	20	10	20
		7 days	0	0	0	0	0	0	0	0	0	0	0	0	20	5	5
		14 days	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0
		21 days	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		Average	0			0.2			0			0			11.4		
	Iris	24 hours	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0
		2 days	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0
		3 days	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0
		4 days	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		7 days	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		14 days	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		21 days	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		Average	0			0.2			0			0			0.7		
	Conjunctiva	24 hours	4	2	2	2	4	2	6	4	6	0	0	0	8	8	6
		2 days	0	0	0	0	0	0	0	0	0	0	0	0	6	4	4
		3 days	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0
		4 days	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0
		7 days	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		14 days	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		21 days	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		Average	0.4			0.4			0.8			0			1.9		

Claims

1. A cyclohexane compound of the general formula:



(I)

wherein (i) R is a hydrogen atom or an alkyl group and then R^1 is an alkyl group, an unsubstituted or substituted benzyl group, a phenethyl group, a phenoxymethyl group or a 2-thienylmethyl group, or (ii) R is an alkylthioalkyl group, a phenyl group or substituted phenyl group and then R^1 is an unsubstituted or substituted benzyl group, a phenethyl group, a phenoxymethyl group or a 2-thienylmethyl group; or a salt of said cyclohexane compound (I) with an inorganic or organic cation; with the proviso that when a compound of formula I is such that R is hydrogen or alkyl and R^1 is alkyl, then said compound is in the form of a salt thereof.

2. A compound according to Claim 1, in which R is a hydrogen atom or an alkyl group.

3. A compound according to Claim 1 in which R^1 is an alkyl group.

4. A compound according to Claim 1 in which both R and R^1 are each an alkyl group of 1—8 carbon atoms.

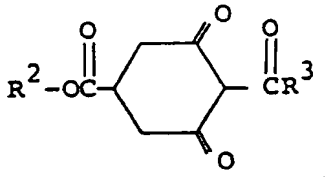
5. A compound according to Claim 1 in which R is an alkyl group which is chosen from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and isopentyl.

6. A compound according to Claim 1 in which R^1 is an alkyl group which is chosen from methyl, ethyl, n-propyl, isopropyl.

7. A compound according to Claim 1 which is a salt of a compound selected from 3,5-dioxo-4-propionylcyclohexanecarboxylic acid methyl ester; 3,5-dioxo-4-propionylcyclohexanecarboxylic acid n-propyl ester; 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid; 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid ethyl ester; 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid n-propyl ester; 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid isopropyl ester; 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid n-butyl ester; 3,5-dioxo-4-butyrylcyclohexanecarboxylic acid isopentyl ester; 3,5-dioxo-4-isobutyrylcyclohexanecarboxylic acid ethyl ester; and 3,5-dioxo-4-acetylcyclohexanecarboxylic acid.

8. A salt of 3,5-dioxo-4-propionylcyclohexanecarboxylic acid ethyl ester.

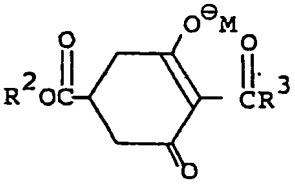
9. A compound as claimed in Claim 1, which is a salt of a cyclohexane compound of the general formula:



(Ia)

wherein R^2 represents a hydrogen atom or an alkyl group and R^3 represents an alkyl group.

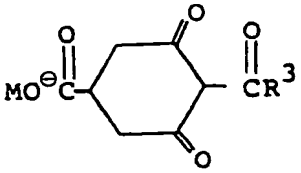
10. A compound according to Claim 9 which is a salt of the cyclohexane compound represented by the general formula:



(Ib)

wherein R^2 and R^3 are as defined in Claim 9 and M represents an organic or inorganic cation.

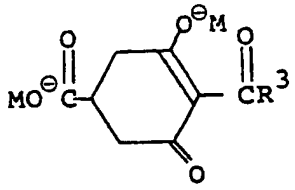
11. A compound according to Claim 9 which is a salt of the cyclohexane compound represented by the general formula:



(Ic)

wherein R^3 is as defined in Claim 9 and M represents an organic or inorganic cation.

12. A compound according to Claim 9 which is a salt of the cyclohexane compound represented by the general formula:



(Id)

wherein R^3 is as defined in claim 9 and M represents an organic or inorganic cation.

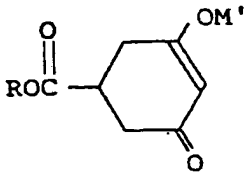
13. A compound according to any one of claims 1 to 12 which is a salt of the cyclohexane compound with an inorganic cation which is selected from cations of an alkali metal, an alkaline earth metal, aluminum, nickel, copper, manganese, cobalt, zinc, iron and silver, as well as ammonium cations.

14. A compound according to any one of claims 1 to 12 which is a salt of the cyclohexane compound of the formula (Ia) with an organic cation which is a substituted ammonium cation, the substituent on the ammonium cation being an alkyl, a hydroxyalkyl, an alkenyl, benzyl, a halo-benzyl, pyridyl, an alkylpyridyl, or a polymethylene link optionally interrupted by an oxygen atom.

15. A compound according to Claim 9, which is chosen from:— [bis-(2-hydroxyethyl)]ammonium salt of ethyl 3,5-dioxo-4-propionyl-cyclohexanecarboxylate; sodium salt of ethyl 3,5-dioxo-4-propionyl-cyclohexanecarboxylate; disodium salt of 3,5-dioxo-4-propionyl-cyclohexanecarboxylic acid; bis-{[bis-(2-hydroxyethyl)]ammonium} salt of 3,5-dioxo-4-propionyl-cyclohexanecarboxylic acid; and [bis-(2-hydroxypropyl)]ammonium salt of ethyl 3,5-dioxo-4-propionyl-cyclohexanecarboxylate.

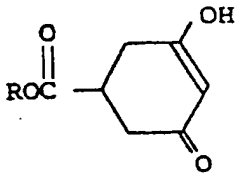
16. A process for the production of a cyclohexane compound as claimed in Claim 1, which comprises the steps of:—

(a) reacting a compound of the formula (III):



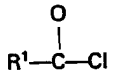
(III)

or a compound of the formula (IV):



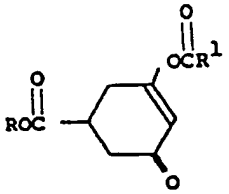
(IV)

wherein R is as defined above and M' is an alkali metal atom, with an organic acid chloride compound of the formula (V):



(V)

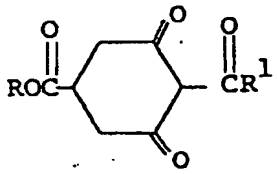
wherein R^1 is as defined above, in an organic solvent and/or water as the reaction medium in the presence or absence of a base as an acid-binding agent to produce the compound of the formula (VI):



(VI)

wherein R and R^1 are as defined above,

(b) subjecting the compound of the formula (VI) to intermolecular rearrangement in the presence of a catalyst which is chosen from 4-N,N-dimethylaminopyridine, 4-N,N-diethylaminopyridine, 4-pyrolidino-aminopyridine, N-methylimidazole, and N-ethylimidazole to produce the compound of the formula (I):



(I)

wherein R and R^1 are as defined above, and

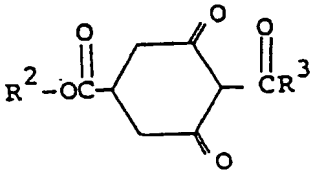
(c) if appropriate, reacting the compound of the formula (I) with an inorganic or organic cation to produce the salt of the compound (I) with said inorganic or organic cation.

17. A process according to Claim 16, in which the step of reacting the compound (III) or (IV) with an organic acid chloride (V) to produce the compound (VI) is carried out in a mixture of water and an organic solvent and in the presence of γ-picoline as a phase transition catalyst.

18. A process according to Claim 16, in which the step of subjecting the compound (VI) to rearrangement to produce the compound (I) is carried out in the presence of 4-N,N-dimethylaminopyridine as the catalyst.

19. A plant-growth regulating composition comprising as active ingredient a cyclohexane compound as defined in claim 1.

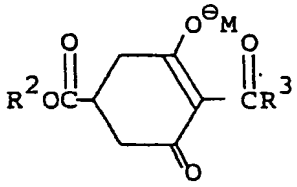
20. A plant-growth regulating composition comprising as active ingredient a salt of a cyclohexane compound having the general formula:



(Ia)

wherein R^2 represents a hydrogen atom or an alkyl group and R^3 represents an alkyl group.

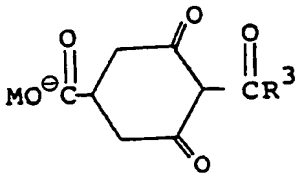
21. A composition according to Claim 20, in which the salt is of the general formula:



(Ib)

wherein R^2 and R^3 are as defined in Claim 20 and M represents an organic or inorganic cation.

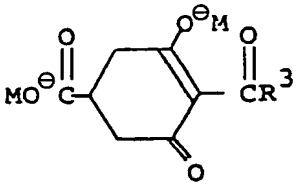
22. A composition according to Claim 20, in which the salt is of the formula:



(Ic)

wherein R^3 and M are as defined in Claim 21.

23. A composition according to Claim 20, in which the salt is of the formula:



(Id)

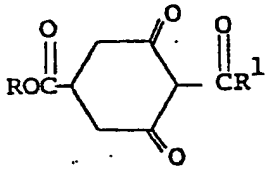
wherein R^3 and M are as defined in claim 21.

24. A method of regulating the growth of plant, which comprises applying an effective amount of a cyclohexane compound of the formula (I) or a salt thereof as claimed in Claim 1 to the foliage or seed of the plant to be treated or to the soil or locus where the plant to be treated is grown.

25. A process for the preparation of a compound as claimed in claim 9, which comprises reacting a compound of formula Ia with an organic or inorganic cation to produce a corresponding salt thereof.

Patentansprüche

1. Cyclohexanverbindung der allgemeinen Formel:



(I)

worin (i) R ein Wasserstoffatom oder eine Alkylgruppe und R^1 dann eine Alkylgruppe, eine unsubstituierte oder substituierte Benzylgruppe, eine Phenethylgruppe, eine Phenoxymethylgruppe oder eine 2-Thienylmethylgruppe ist oder (ii) R eine Alkylthioalkylgruppe, eine Phenylgruppe oder substituierte Phenylgruppe ist und R^1 dann eine unsubstituierte oder substituierte Benzylgruppe, eine Phenethylgruppe, eine Phenoxymethylgruppe oder eine 2-Thienylmethylgruppe ist, oder eine Salz der Cyclohexanverbindung (I) mit einem anorganischen oder organischen Kation, mit der Maßgabe, daß wenn eine Verbindung der formel I derart ist, daß R Wasserstoff oder Alkyl ist und R^1 Alkyl ist, die Verbindung dann in Form eines Salzes davon vorliegt.

2. Verbindung nach Anspruch 1, worin R ein Wasserstoffatom oder eine Alkylgruppe ist.

3. Verbindung nach Anspruch 1, worin R^1 eine Alkylgruppe ist.

4. Verbindung nach Anspruch 1, worin R als auch R^1 jeweils eine Alkylgruppe mit 1—8 Kohlenstoffatomen ist.

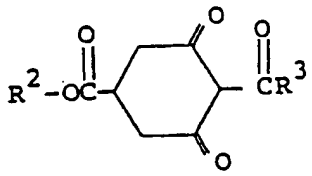
5. Verbindung nach Anspruch 1, worin R eine Alkylgruppe, ausgewählt unter Methyl, Ethyl, n-Propyl, Isopropyl, n-Butyl, Isobutyl and Isopentyl ist.

6. Verbindung nach Anspruch 1, worin R^1 eine Alkylgruppe ausgewählt unter Methyl, Ethyl, n-Propyl, Isopropyl, ist.

7. Verbindung nach Anspruch 1, die ein Salz einer Verbindung ist, ausgewählt unter 3,5-Dioxo-4-propionylcyclohexankarbonsäuremethylester, 3,5-Dioxo-4-propionylcyclohexankarbonsäure-n-propylester, 3,5-Dioxo-4-butyrylcyclohexankarbonsäure, 3,5-Dioxo-4-butyrylcyclohexankarbonsäureethylester, 3,5-Dioxo-4-butyrylcyclohexankarbonsäure-n-propylester, 3,5-Dioxo-4-butyrylcyclohexankarbonsäureisopropylester, 3,5-Dioxo-4-butyrylcyclohexankarbonsäure-n-butylester, 3,5-Dioxo-4-butyrylcyclohexankarbonsäureisopentylester, 3,5-Dioxo-4-isobutyrylcyclohexankarbonsäureethylester und 3,5-Dioxo-4-acetylcyclohexankarbonsäure.

8. Salz von 3,5-Dioxo-4-propionylcyclohexankarbonsäureethylester.

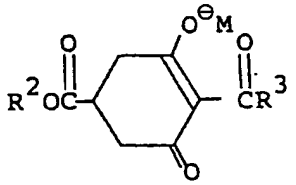
9. Verbindung nach Anspruch 1, die ein Salz einer Cyclohexanverbindung der allgemeinen Formel:



(Ia)

ist, worin R^2 ein Wasserstoffatom oder eine Alkylgruppe und R^3 eine Alkylgruppe darstellt.

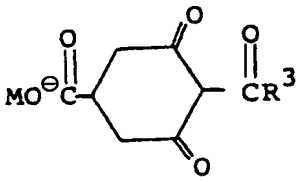
10. Verbindung nach Anspruch 9, die eine Salz der Cyclohexanverbindung, dargestellt durch die allgemeine Formel:



(Ib)

ist, worin R^2 und R^3 wie in Anspruch 9 definiert sind und M ein organisches oder anorganisches Kation darstellt.

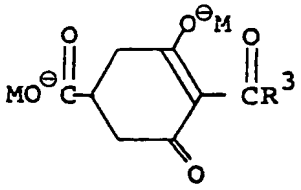
11. Verbindung nach Anspruch 9, die ein Salz der Cyclohexanverbindung, dargestellt durch die allgemeine Formel



(Ic)

ist, worin R^3 wie in Anspruch 9 definiert ist und M ein organisches oder anorganisches Kation darstellt.

12. Verbindung nach Anspruch 9, die ein Salz der Cyclohexanverbindung, dargestellt durch die allgemeine Formel



(Id)

ist, worin R^3 wie in Anspruch 9 definiert ist und M ein organisches oder anorganisches Kation darstellt.

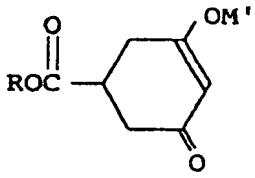
13. Verbindung nach einem der Ansprüche 1 bis 12, die ein Salz der Cyclohexanverbindung mit einem anorganischen Kation ist, ausgewählt unter Kationen eines Alkalimetalls, eines Erdalkalimetalls, Aluminium, Nickel, Kupfer, Mangan, Kobalt, Zink, Eisen und Silber, als auch unter Ammoniumkationen.

14. Verbindung nach einem der Ansprüche 1 bis 12, die ein Salz der Cyclohexanverbindung der Formel (Ia) mit einem organischen Kation ist, das ein substituiertes Ammoniumkation ist, wobei der Substituent an dem Ammoniumkation eine Alkyl-, hydroxyalkyl-, Alkenyl-, Benzyl-, Halo-benzyl-, Pyridyl-, Alkylpyridyl oder eine Polymethylenkette, gegebenenfalls, unterbrochen durch ein Sauerstoffatom, ist.

15. Verbindung nach Anspruch 9, ausgewählt unter [Bis-(2-hydroxyethyl)]ammoniumsalz von Ethyl-3,5-dioxo-4-propionyl-cyclohexankarboxylat, Natriumsalz von Ethyl-3,5-dioxo-4-propionyl-cyclohexankarboxylat, Dinatriumsalz von 3,5-Dioxo-4-propionyl-cyclohexankarbonsäure, Bis-{[bis-(2-hydroxyethyl)] amonium]salz von 3,5-Dioxo-4-propionyl-cyclohexankarbonsäure und [Bis-(2-hydroxypropyl)]ammonium-salz von Ethyl-3,5-dioxo-4-propionyl-cyclohexankarboxylat.

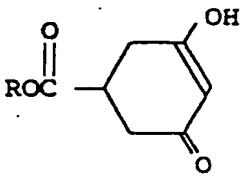
16. Verfahren zur Herstellung einer Cyclohexanverbindung nach Anspruch 1, das die folgenden Schritte umfaßt:

(a) Imsetzen einer Verbindung der Formel (III)



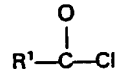
(III)

oder einer Verbindung der Formel (IV)



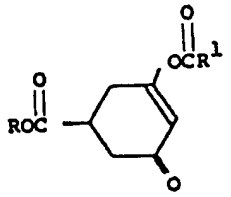
(IV)

worin R wie oben definiert und M' ein Alkalimetallatom ist, mit einer organischen, Säurechloridverbindung der Formel (V)



(V)

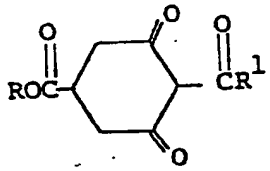
worin R^1 wie oben definiert ist, in einem organischen Lösungsmittel und/oder Wasser als Reaktionsmedium in Anwesenheit oder Abwesenheit einer Base als säurebindendes Mittel zur Herstellung der Verbindung der Formel (VI)



(VI)

worin R und R^1 wie oben definiert sind

(b) die Verbindung der Formel (VI) eine intermolekularen Umgruppierung unterziehen, in Anwesenheit eines Katalysators, der ausgewählt ist unter 4-N,N-dimethylaminopyridin, 4-N,N-diethylaminopyridin, 4-Pyrrolidinoaminopyridin, N-methylimidazol und N-ethylimidazol zur Herstellung der Verbindung der Formel (I)



(I)

worin R und R^1 wie oben definiert sind, und

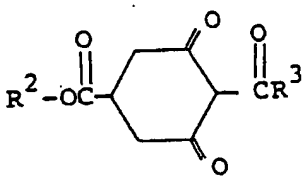
(c) falls geeignet, Umsetzen der Verbindung der Formel (I) mit einem anorganischen oder organischen Kation zur Herstellung des Salzes der Verbindung (I) mit diesem anorganischen oder organischen Kation.

17. Verbindung nach Anspruch 16, in welchem der Schritt der Umsetzung der Verbindung (III) oder (IV) mit einem organischen, Säurechlorid (V) zur Herstellung der Verbindung (VI) in einer Mischung von Wasser und einem organischen Lösungsmittel und in Anwesenheit von γ-Pikolin als eine Phasenübergangskatalysator durchgeführt wird.

18. Verbindung nach Anspruch 16, worin der Schritt, bei dem die Verbindung (VI) einer Umlagerung unterworfen wird zu Herstellung der Verbindung (I) in Anwesenheit von 4-N,N-dimethylaminopyridin als Katalysator durchgeführt wird.

19. Pflanzenwachstum regulierende Zusammensetzung, umfassend als aktiven Bestandteil eine Cyuclohexanverbindung wie in Anspruch 1 definiert.

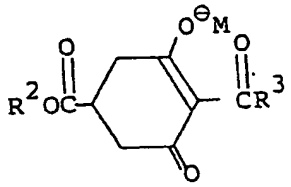
20. Pflanzenwachstum regulierende Zusammenzetzung, umfassend als aktiven Bestandteil ein Salz einer Cyclohexanverbindung der allgemeinen Formel



(Ia)

worin R^2 ein Wasserstoffatom oder eine Alkylgruppe und R^3 eine Alkylgruppe darstellt.

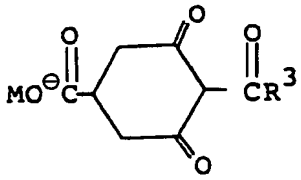
21. Zusammensetzung nach Anspruch 20, worin das Salz die allgemeine Formel



(Ib)

aufweist, worin R^2 und R^3 wie in Anspruch 20 definiert sind und M ein organisches oder anorganisches Kation darstellt.

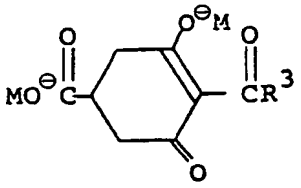
22. Zusammensetzung nach Anspruch 20, worin das Salz die Formel



(Ic)

aufweist, worin R^3 und M wie in Anspruch 21 definiert sind.

23. Zusammensetzung nach Anspruch 20, worin das Salz die Formel



(Id)

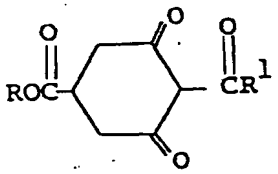
aufweist, worin R^3 und M wie in Anspruch 21 definiert sind.

24. Verfahren zur Regulation des Pflanzenwachstums, umfassend das Auftragen einer wirksamen Menge einer Cyclohexanverbindung der Formel (I) oder eines Salzes davon gemäß Anspruch 1 auf das Laub oder den Samen der zu behandelnden Pflanze oder aus den Boden oder Standort auf dem die zu behandelnde Pflanze wachsen soll.

25. Verfahren zur Herstellung einer Verbindung nach Anspruch 9, umfassend das Umsetzen einer Verbindung der Formel Ia mit einem organischen oder anorganischen Kation zur Herstellung eines entsprechenden Salzes davon.

Revendications

1. Dérivé de cyclohexane de formule générale:



(I)

dans laquelle (i) R est un un atome d'hydrogène ou un groupe alkyle et R^1 est alors un groupe alkyle, un groupe benzyle non substitué ou substitué, un groupe phénéthyle, un groupe phénoxyméthyle ou un groupe 2-thiénylméthyle, ou (ii) est un groupe alkylthioalkyle, un groupe phényle ou un groupe phényle substitué et R^1 est alors un groupe benzyle non substitué ou substitué, un groupe phénéthyle, un groupe phénoxyméthyle ou un groupe 2-thiénylméthyle; ou un sel dudit dérive de cyclohexane (I) à cation minéral ou organique; sous réserve que, lorsqu'un composé de formule I est tel que R est un hydrogène ou un alkyle et R^1 est un alkyle, ledit composé soit sous forme d'un sel.

2. Composé selon la revendication 1, dans lequel R est un atome d'hydrogène ou un groupe alkyle.

3. Composé selon la revendication 1, dans lequel R^1 est un groupe alkyle.

4. Composé selon la revendication 1, dans lequel R et R^1 sont chacun un groupe alkyle de 1 à 8 atomes de carbone.

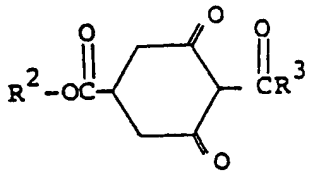
5. Composé selon la revendication 1, dans lequel R est un groupe alkyle choisi parmi méthyle, éthyle, n-propyle, isopropyle, n-butyle, isobutyle et isopentyle.

6. Composé selon la revendication 1, dans lequel R^1 est un groupe alkyle choisi parmi méthyle, éthyle, n-propyle et isopropyle.

7. Composé selon la revendication 1, qui est sel d'un composé choisi parmi l'ester méthylique de l'acide 3,5-dioxo-4-propionylcyclohexanecarboxylique; l'ester n-propylique de l'acide 3,5-dioxo-4-propionylcyclohexanecarboxylique; l'acide 3,5-dioxo-4-butyrylcyclohexanecarboxylique; l'ester éthylique de l'acide 3,5-dioxo-4-butyrylcyclohexanecarboxylique; l'ester n-propylique de l'acide 3,5-dioxo-4-butyrylcyclohexanecarboxylique; l'ester isopropylique de l'acide 3,5-dioxo-4-butyrylcyclohexanecarboxylique; l'ester n-butylique de l'acide 3,5-dioxo-4-butyrylcyclohexanecarboxylique; l'ester isopentylique de l'acide 3,5-dioxo-4-butyrylcyclohexanecarboxylique; l'ester éthylique de l'acide 3,5-dioxo-4-isobutyrylcyclohexanecarboxylique; et l'acide 3,5-dioxo-4-acétylcyclohexanecarboxylique.

8. Sel de l'ester éthylique de l'acide 3,5-dioxo-4-propionylcyclohexanecarboxylique.

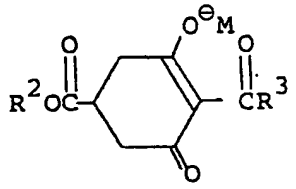
9. Composé selon la revendication 1 qui est un sel d'un dérivé de cyclohexane de formule générale:



(Ia)

dans laquelle R^2 représente un atome d'hydrogène ou un groupe alkyle et R^3 représente un groupe alkyle.

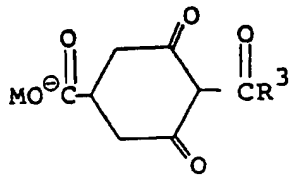
10. Composé selon la revendication 9 qui est un sel du dérivé de cyclohexane représenté par la formule générale:



(Ib)

dans laquelle R^2 et R^3 sont définis comme dans la revendication 9 et M représente un cation organique ou minéral.

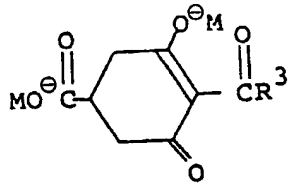
11. Composé selon la revendication 9, qui est un sel du dérivé de cyclohexane représenté par la formule générale:



(Ic)

dans laquelle R^3 est défini comme dans la revendication 9 et M représente un cation organique ou minéral.

12. Composé selon la revendication 9 qui est un el du dérivé de cyclohexane représenté par la formule générale:



(Id)

dans laquelle R^3 est défini comme dans la revendication 9 et M représente un cation organique ou minéral.

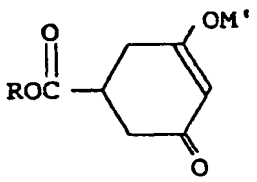
13. Composé selon l'une quelconque des revendications 1 à 12 qui est un sel du dérivé de cyclohexane à cation minéral qui est choisi parmi les cations de métal alcalin, de métal alcalinoterreux, d'aluminium, de nickel, de cuivre, de manganèse, de cobalt, de zinc, de fer, d'argent et d'ammonium.

14. Composé selon l'une quelconque des revendications 1 à 12 qui est un sel du dérivé de cyclohexane de formule (Ia) à cation organique qui est un cation ammonium substitué, le substituant du cation ammonium étant un alkyle, un hydroxyalkyle, un alcényle, un benzyle, un halogénobenzyle, un pyridyle, un alkylpyridyle ou une chaîne polyméthylène éventuellement interrompue par un atome d'oxygène.

15. Composé selon la revendication 9 choisi parmi: le sel de [bis-(2-hydroxyéthyl)]ammonium du 3,5-dioxo-4-propionylcyclohexanecarboxylate d'éthyle; le sel de sodium du 3,5-dioxo-4-propionylcyclohexanecarboxylate d'éthyle; le sel disodique de l'acide 3,5-dioxo-4-propionylcyclohexane-carboxylique; le sel de bis-{[bis-(2-hydroxyéthyl)]ammonium} de l'acide 3,5-dioxo-4-propionylcyclo-hexanecarboxylique; et le sel de [bis-(2-hydroxypropyl)]ammonium du 3,5-dioxo-4-propionylcyclohexane-carboxylate d'éthyle.

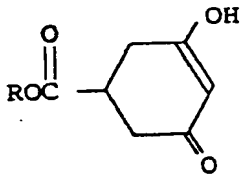
16. Procédé pour la production d'un dérivé de cyclohexane selon la revendication 1, qui comprend les étapes consistant à:

(a) faire réagir un composé de formule (III):



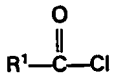
(III)

ou un composé de formule (IV):



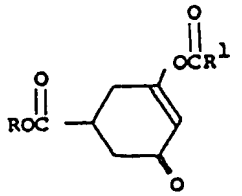
(IV)

dans lesquelles R est défini comme ci-dessus et M' est un atome de métal alcalin, avec un chlorure d'acide organique de formule (V):



(V)

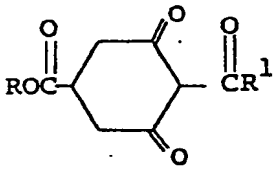
dans laquelle R^1 est défini comme ci-dessus, dans un solvant organique et/ou l'eau comme milieu réactionnel, en présence ou en l'absence d'un base comme agent fixant les acides, pour produire le composé de formule (VI):



(VI)

dans laquelle R et R^1 sont définis comme ci-dessus,

(b) soumettre le composé de formule (VI) à une transposition intermoléculaire en présence d'un catalyseur choisi parmi la 4-N,N-diméthylaminopyridine, la 4-N,N-diéthylaminopyridine, la 4-pyrrolidinoaminopyridine, le N-méthylimidazole, et le N-ethylimidazole, pour produire le composé de formule (I):



(I)

dans laquelle R et R^1 sont définis comme ci-dessus, et

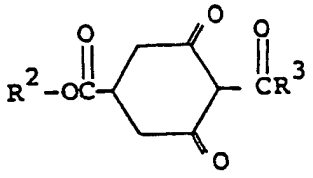
(c) le cas échéant, faire réagir le composé de formule (I) avec un cation minéral ou organique pour produire le sel du composé (I) ayant ledit cation minéral ou organique.

17. Procédé selon la revendication 16, dans lequel l'étape de réaction du composé (III) ou (IV) avec un chlorure d'acide organique (V) pour produire le composé (VI) est effectuée dans un mélange d'eau et d'un solvant organique et en présence de γ-picoline comme catalyseur de transition de phase.

18. Procédé selon la revendication 16, dans lequel l'étape consistant à soumettre le composé (VI) à une transposition pour produire le composé (I) est effectuée en présence de 4-N,N-diméthylaminopyridine comme catalyseur.

19. Composition régulatrice de la croissance des plantes comprenant comme ingrédient actif un dérivé de cyclohexane comme défini dans la revendication 1.

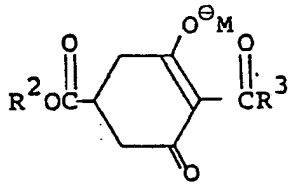
20. Composition régulatrice de la croissance des plantes comprenant comme ingrédient actif un sel d'un dérivé de cyclohexane répondant à la formule générale:



(Ia)

dans laquelle R^2 représente un atome d'hydrogène ou un groupe alkyle et R^3 représente un groupe alkyle.

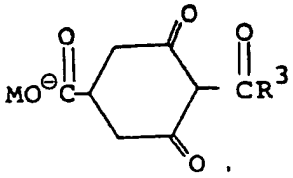
21. Composition selon la revendication 20, dans laquelle le sel répond à la formule générale:



(Ib)

dans laquelle R^2 et R^3 sont définis comme dans la revendication 20 et M représente un cation organique ou minéral.

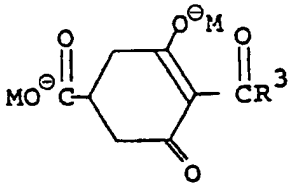
22. Composition selon la revendication 20, dans laquelle le sel répond à la formule:



(Ic)

dans laquelle R^3 et M sont définis comme dans la revendication 21.

23. Composition selon la revendication 20, dans laquelle le sel répond à la formule:



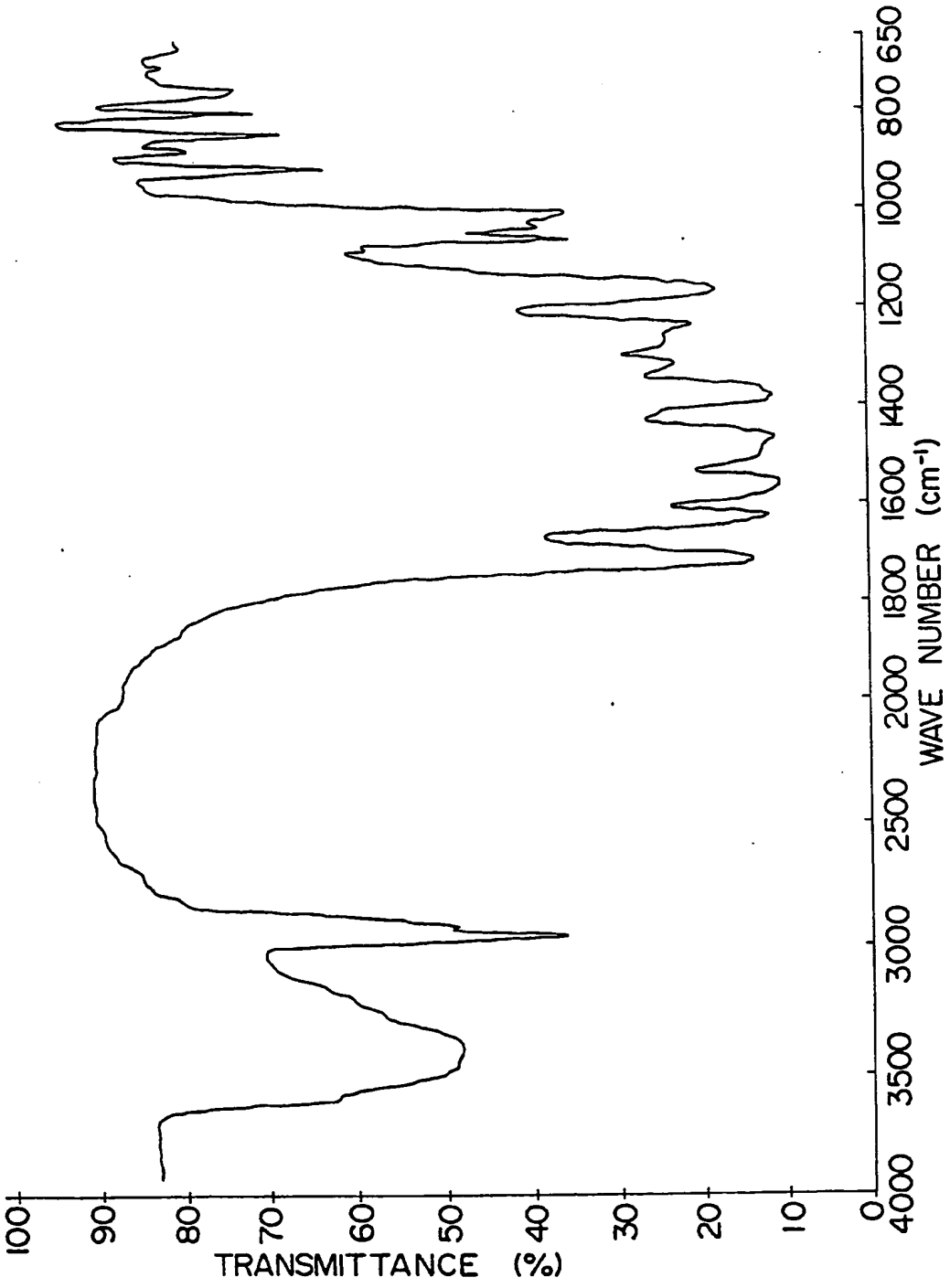
(Id)

dans laquelle R^3 et M sont définis comme dans la revendication 21.

24. Procédé de régulation de la croissance les plantes qui comprend l'application d'une quantité efficace d'un dérivé de cyclohexane de formule (I) ou d'un de ses sels, tel que défini dans la revendication 1, sur le feuillage ou les graines, de la plante à traiter ou sur le sol ou site où la plante à traiter est cultivée.

25. Procédé pour la préparation d'un composé selon la revendication 9, qui comprend le réaction d'un composé de formule (Ia) avec un cation organique ou minéral pour produire un sel correspondant.

FIG. 1


TRANSMITTANCE (%)
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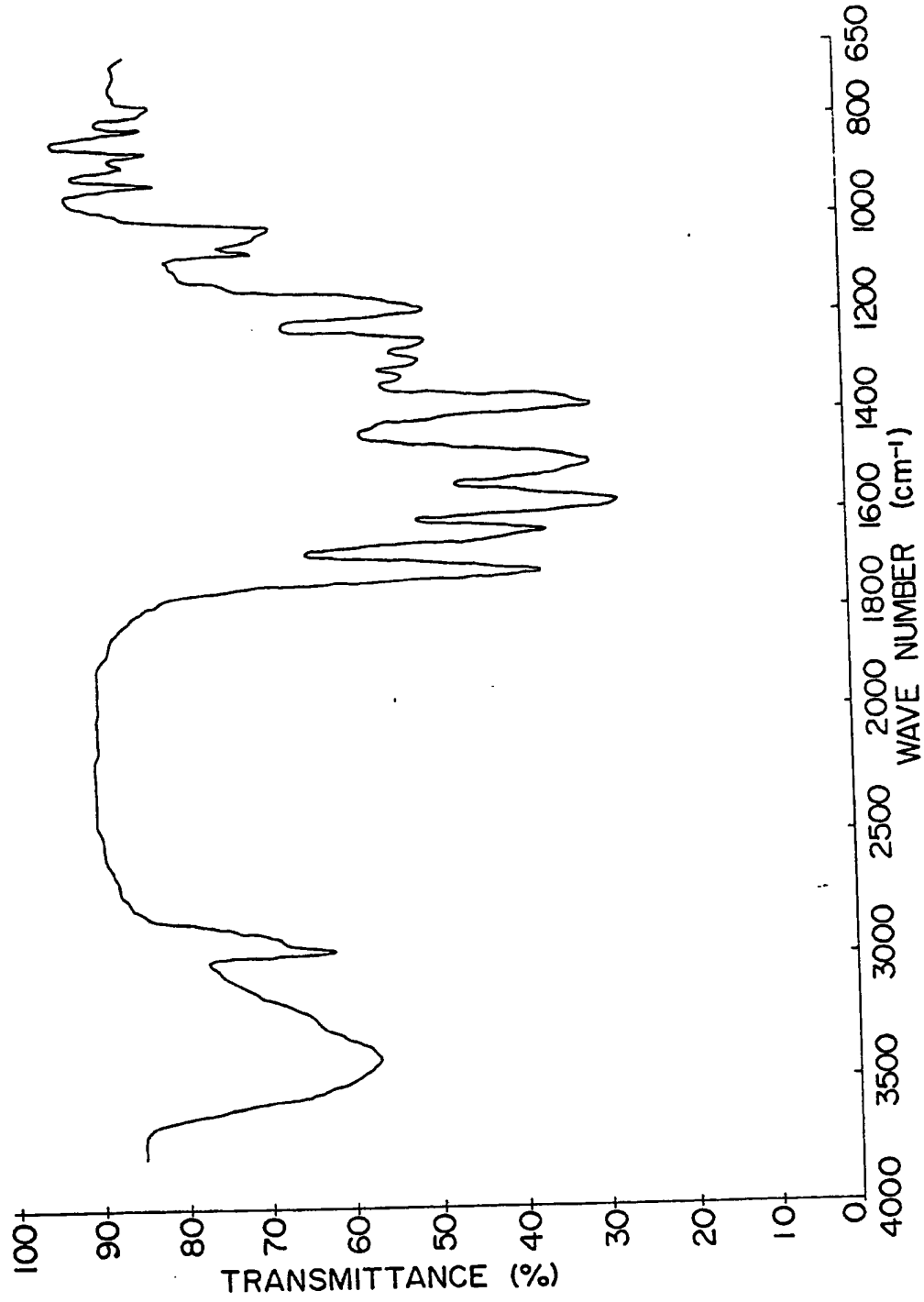
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
650
WAVE NUMBER (cm⁻¹)

FIG.2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90
80
70
60
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30
20
10
0
TRANSMITTANCE (%)
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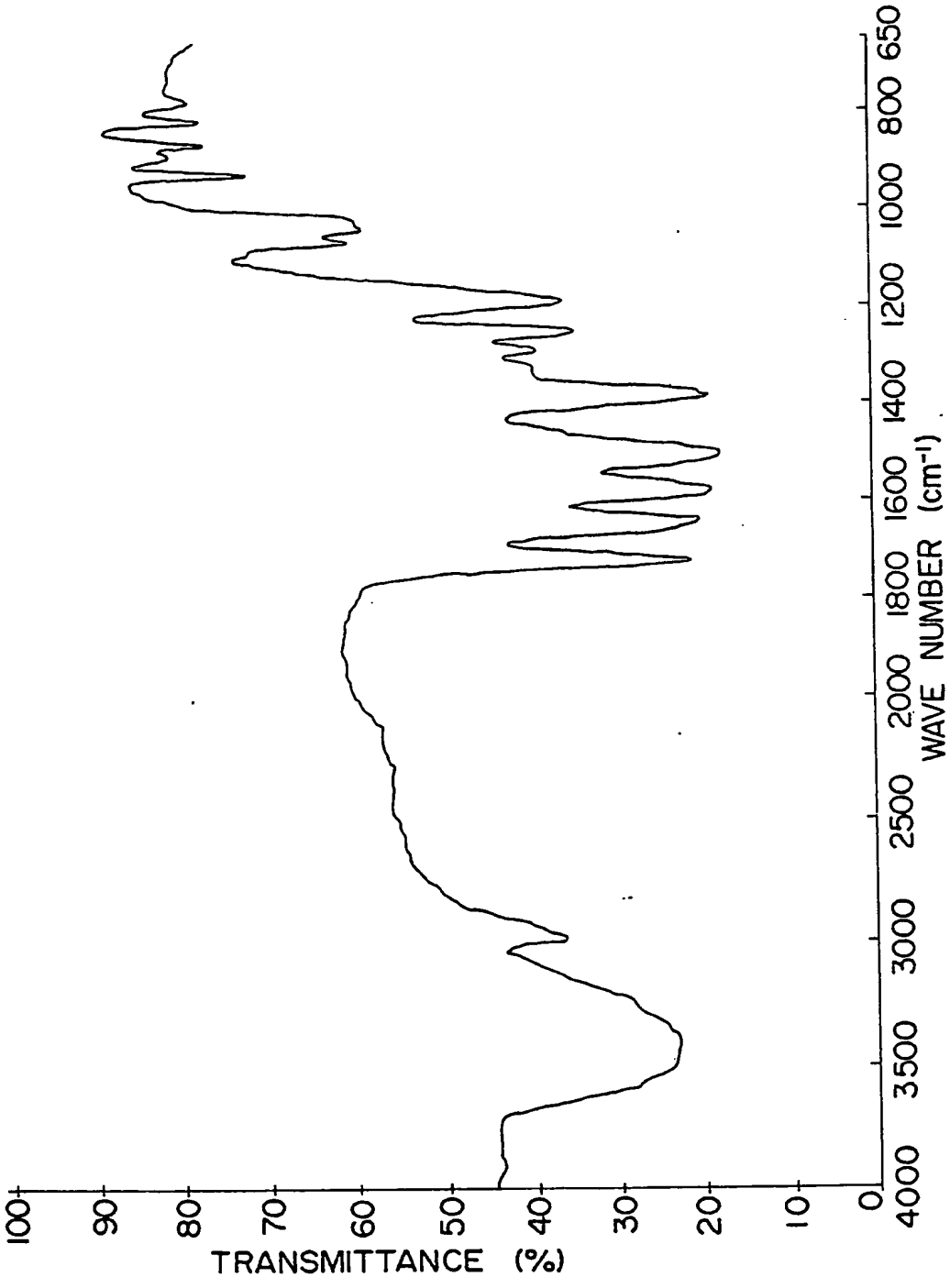
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
650
WAVE NUMBER (cm⁻¹)

FIG.3


TRANSMITTANCE (%)
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1600
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1200
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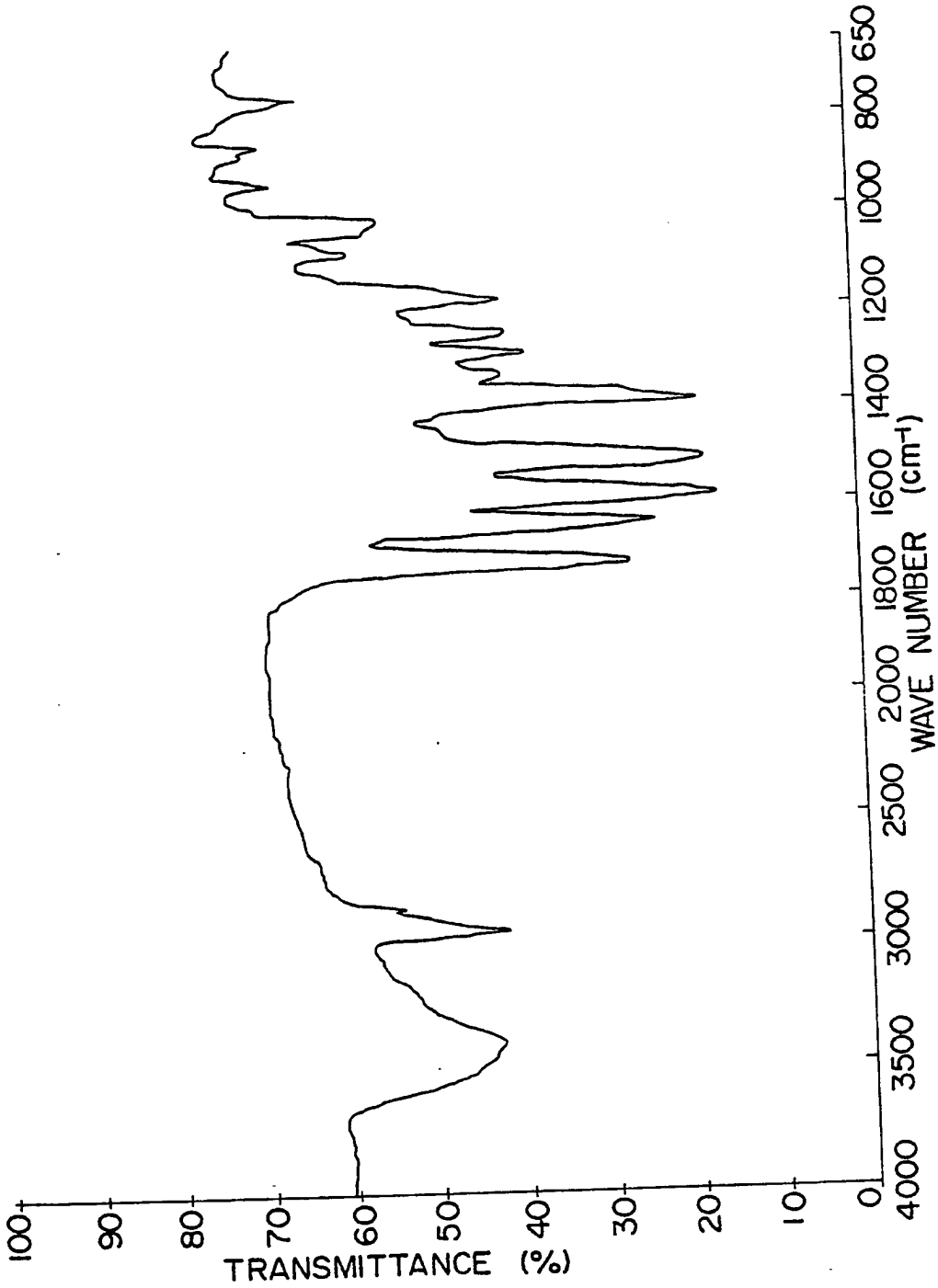
650
WAVE NUMBER (cm⁻¹)

FIG.4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10
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TRANSMITTANCE (%)
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2000
1800
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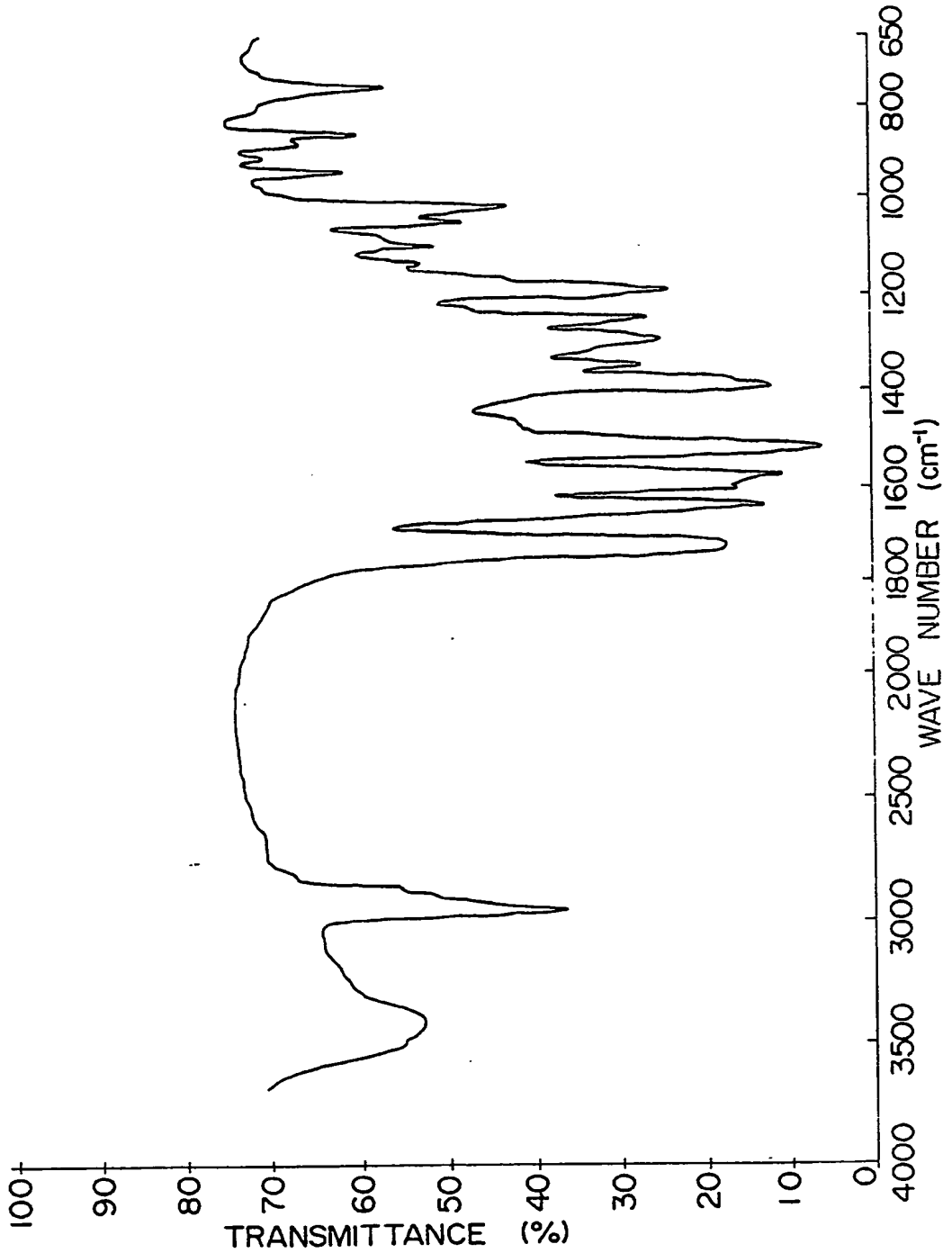
800
650
WAVE NUMBER (cm⁻¹)

FIG. 5


TRANSMITTANCE (%)
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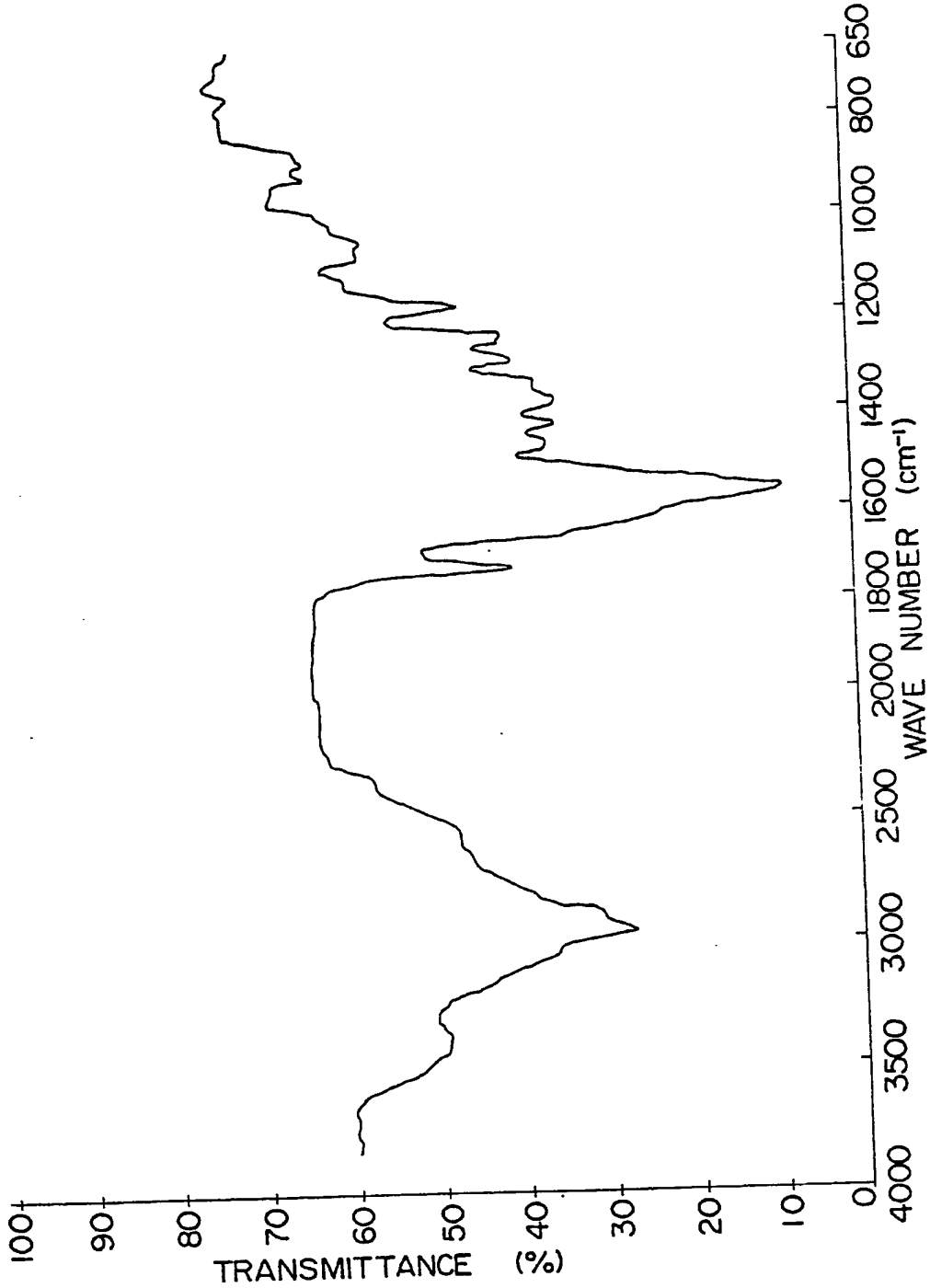
1200
1000
800
650
WAVE NUMBER (cm-1)

FIG.6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10
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TRANSMITTANCE (%)
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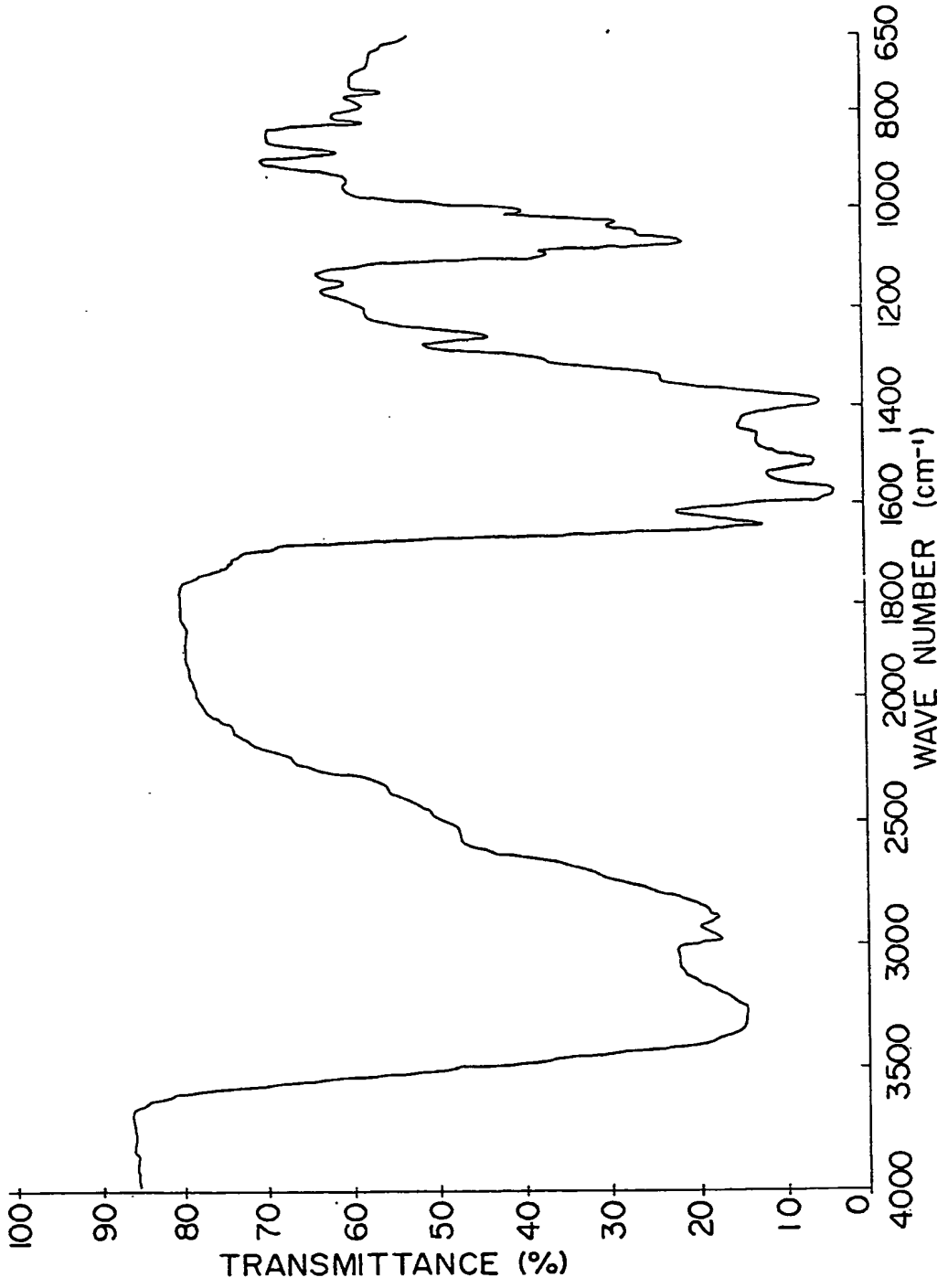
650
WAVE NUMBER (cm⁻¹)

FIG. 7


TRANSMITTANCE (%)
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1600
1400
1200
1000
800
650
WAVE NUMBER (cm⁻¹)